WL-TR-96-3132

ADVANCED STREAMING AGENT DEVELOPMENT, VOLUME IV: TROPODEGRADABLE HALOCARBONS

FINAL REPORT FOR VOL IV

Everett W. Heinonen
Joseph L. Lifke
Robert E. Tapscott

Center for Global Environmental technologies
New Mexico Engineering Research Institute
The University of New Mexico
901 University Boulevard SE
Albuquerque, New Mexico 87106-4339

MAY 1996

INTERIM REPORT FOR AUGUST 1995 TO MARCH 1996

19970213 013

DTIC QUALITY INSPECTED 4

FLIGHT DYNAMICS DIRECTORATE
WRIGHT LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7562

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	MAY 1996	INTERIM, AUGUST 1995--MARCH 1996

4. TITLE AND SUBTITLE
ADVANCED STREAMING AGENT DEVELOPMENT, VOLUME IV:
TROPODEGRADABLE HALOCARBONS

5. FUNDING NUMBERS
F0863593-C-0020
PE: 6.1

6. AUTHOR(S)
Everett W. Heinonen, Joseph L. Lifke, and Robert E. Tapscott

S-5000.31

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

New Mexico Engineering Research Institute
University of New Mexico
Albuquerque, NM 87131-1376

8. PERFORMING ORGANIZATION REPORT NUMBER

NMERI 96/4/32540

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Flight Dynamics Directorate   Wright Laboratories
Wright Laboratory   132 Barnes Drive Ste 2
Air Force Materiel Command   Infrastructure Technology Section
Wright-Patterson AFB OH 45433-7562   Tyndall AFB FL 32403-5323
POC: Major Tetla, WL/FIVCF, Tyndall AFB FL, DSN 523-3745

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

WL-TR-96-3132

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The objective of the overall effort is to develop new chemical compounds as Halon 1211 replacements. Four families of compounds are particularly promising—phosphorus nitrides, metal compounds, silicon compounds, and tropodegradable halocarbons. This report is Volume IV of a 5-volume series of reports. Volume I covers silicon compounds; Volume II, metal compounds; Volume III, phosphorus compounds; and Volume V, laboratory-scale streaming tests. This document assesses tropodegradable halocarbons as candidates as Halon 1211 substitutes.

14. SUBJECT TERMS
Halon 1211; halon replacement; tropodegradable; alkenes; polar; advanced agent; streaming agent; rainout

15. NUMBER OF PAGES
152

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

Standard Form 298 (Rev. 2-89) (EG)
Prescribed by ANSI Std. 239.18
Designed using Perform Pro, WHS/DIOR, Oct 94

i

CONTENTS

CONTENTS (CONTINUED)

CONTENTS (CONCLUDED)

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
ACGIH	American Conference of Governmental Industrial Hygienists
AD_{50}	concentration at which 50 percent of test animals experience anesthesia
AEL	Acceptable Exposure Limit
AIHA	American Industrial Hygiene Association
ALC	Approximate Lethal Concentration
ARA	Applied Research Associates
BFC	bromofluorocarbon
BP	boiling point
CAS	Chemical Abstracts Service
CFC	chlorofluorocarbon
CGET	Center for Global Environmental Technologies
CL	Ceiling Level
CNS	central nervous system
DMF	dimethylformamide
DMSO	dimethylsulfoxide
ECF	electrochemical fluorination
EGL	Emergency Guidance Level
EPA	Environmental Protection Agency
FC	(per)fluorocarbon
FE	(per)fluoroether
GWP	Global Warming Potential
HCFC	hydrochlorofluorocarbon
HFA	hydrofluoroamine
HBFA	hydrobromofluoroamine
HBFC	hydrobromofluorocarbon
HBFE	hydrobromofluoroether
HFC	hydrofluorocarbon
HFE	hydrofluoroether
HR	SAX Hazard Rating

IDLH	Immediately Dangerous to Life and Health
IR	infrared
LC_{LO}	lowest concentration causing death
LC_{50}	concentration required to cause death in 50 percent of an animal test population
LD_{LO}	lowest dose causing death
LD_{50}	dose required to cause death in 50 percent of an animal test population
LEL	lower explosive limit
LFL	lower flammability limit
LOAEL	Lowest Observed Adverse Effect Level
LSDE	Laboratory-Scale Discharge Extinguishment
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NMERI	New Mexico Engineering Research Institute
NMR	nuclear magnetic resonance
NOAEL	No Observed Adverse Effect Level
NRL	Naval Research Laboratory
ODP	Ozone Depletion Potential
ODS	Ozone Depleting Substance
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PEL	Permissible Exposure Limit
PFC	perfluorocarbon
PFA	perfluoroamine
PFE	perfluoroether
REL	Recommended Exposure Limit
SNAP	Significant New Alternatives Policy
STEL	Short-Term Exposure Limit
TC_{LO}	lowest concentration having a toxic effect
TD_{LO}	lowest dose having a toxic effect

LIST OF ABBREVIATIONS (CONCLUDED)

TLV   Threshold Limit Value

UEL   upper explosive limit

USAF   United States Air Force

UV   ultraviolet

WEEL   Workplace Environmental Exposure Limit Guide

WGL   Workplace Guidance Level

LIST OF UNITS AND SYMBOLS

Ar	aryl group
atm	atmosphere (760 Torr)
cm	centimeter
cp	centipoise
c_n	coefficient in heat capacity polynomial (n = 0, 1, 2, 3)
C_p	heat capacity at constant pressure
C_t	concentration at any time t
C_o	initial concentration
d	differential
D	molecular diffusivity of a gas in water
e	base of "natural" logarithmic system (2.71828...)
h	Planck's constant
hr	hour
I	solar intensity
K	Kelvin
k	reaction rate constant
k_1	first-order reaction rate constant
k_{OH}	second-order rate constant for reaction with hydroxyl free radicals
k_{O3}	second-order rate constant for reaction with tropospheric ozone
k_{photo}	first-order photodissociation rate constant
$k_{physical}$	rate constant for physical removal
kg	kilogram
kJ	kilojoules
kJ/mol	kilojoules per mole
km	kilometer
ln	logarithm to the base e
m	meter
mg	milligram
min	minute

mm	millimeter
nm	nanometer
N_F	number of fluorine atoms in a molecule
N_H	number of hydrogen atoms in a molecule
p	partial pressure
ppb	parts per billion
ppm	parts per million
P_{vap}	vapor pressure
R	gas constant; organic group (usually an alkyl or halogenated alkyl group)
R_f	fluorinated or partially fluorinated alkyl group
s	second
t	time
$t_{1/e}$	e-folding atmospheric lifetime
$t_{1/2}$	atmospheric half life
T	temperature
Torr	mm of mercury pressure
W	watt
X	halogen atom
Y	a hydrogen or halogen substituent
z	film thickness in the classical stagnant film model for gas exchange
α	solubility coefficient
β	Henry's law constant in moles/m^3-atm
hν	represents a photon in a photolysis reaction
[B]	concentration of a chemical species B
•OH	hydroxyl free radical
•	denotes a free radical, e.g., •R is a free radical of an organic group
λ	wavelength

LIST OF UNITS AND SYMBOLS (CONCLUDED)

μg	microgram
ν	frequency
φ	photodissociation quantum yield
σ	absorption cross section

A.   OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

This document is Volume IV of the final report and provides an assessment of tropodegradable halocarbons as potential substitutes for replacement of Halon 1211 in streaming applications. The five volumes of the final report are listed below:

Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/1/32540

Patterson, R. A., Gobeli, G. W., Brabson, G. D., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume II: Metal Compounds*, WL-TR-96-XX, Vol. 2 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/3/32540

Kaizerman, J. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume III: Phosphorus Compounds*, WL-TR-96-XX, Vol. 3 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/5/32540

Heinonen, E. W., Lifke, J. L., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons*, WL-TR-96-XX, Vol. 4 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/4/32540

Lifke, J. L., Moore, T. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests*, WL-TR-96-XX, Vol. 5 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/2/32540

B. BACKGROUND

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of the fire and explosion protection agents Halon 1211 (bromochlorodifluoromethane, BCFC-12B1, $CBrClF_2$) and Halon 1301 (bromotrifluoromethane, BFC-13B1, $CBrF_3$) was phased out in the United States at the end of 1993.[*] To date, no environmentally acceptable halon substitute that is equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified.

Halocarbons as replacements for halons have been well studied, and it is unlikely that new, exceptionally effective, halon replacements will be identified among the standard, saturated, non-iodinated halocarbons. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios and usually exhibit higher toxic gas emissions during fire suppression. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs. The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide (CF_3I), which is as effective as the existing halons. However, the cardiosensitization by the fluoroalkyl iodides that have been investigated restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the usual, saturated halocarbons. These compounds are the non-halocarbon candidates, known as "advanced agents." The most promising of these are the phosphorus compounds (particularly, the phosphorus nitrides, which include phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds.

---

[*]See Appendix A for an overview of halocarbon numbers (e.g., "BCFC-12B1" and "BFC-13B1") and general information on halocarbon nomenclature.

In addition, the special class of tropodegradable halocarbons, the subject of this report, includes promising candidates.

C.   SCOPE

An investigation of advanced fire suppression agents is being conducted to find a replacement for Halon 1211 used in Air Force flightline and aircraft portable fire extinguishers. Four separate tasks are included in the overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal complexes, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

Task 2: Synthesis of New Compounds. Samples of the most promising of these materials based on expected toxicity, availability/manufacturability, and environmental characteristics are to be prepared or obtained.

Task 3: Laboratory Evaluations. Laboratory-scale evaluations of fire extinguishment by these materials are to be performed. Preliminary analyses of global environmental impact, toxicity evaluations, and manufacturing/synthesis assessment of the candidates identified for follow-on testing are to be conducted.

Task 4: Final Report. The information obtained is to be used to prepare a final report detailing the work performed, the results obtained, and conclusions. The report will make recommendations for continuation of large-scale testing with the most promising agents.

D.   METHODOLOGY

The rationale is to use bromocarbons with extremely short atmospheric lifetimes (tropodegradable halocarbons). The term "tropodegradable" is used here for any halocarbon with an atmospheric lifetime on the order of days or weeks. Tropodegradable halocarbons help solve three environmental problems — ozone depletion, global warming, and atmospheric lifetime. If

the atmospheric lifetimes are similar to those of the iodides (which appear to have received environmental acceptance), and the market potential is small (halon replacement only), such compounds may be environmentally acceptable. Existing models are used to determine the atmospheric lifetimes and to make predictions of global environmental impacts.

E.   APPROACH

The rates of photolysis, hydroxyl free radical reactions, reactions with tropospheric ozone, and contributions from physical removal processes are used to estimate atmospheric lifetimes for compounds of interest. From this information, the potential of each family as halon replacement substitutes is assessed.

F.   RESULTS

Assessment of tropospheric sinks indicates four mechanisms of importance for the compounds of interest here: (1) reaction with atmospheric hydroxyl free radicals; (2) photolysis; (3) physical removal; and (4) reaction with tropospheric ozone. An overall pseudo first-order rate constant k_1 can be written, where $k_1 = k_{OH}[\bullet OH] + k_{physical} + k_{photo} + k_{O3}[O_3]$. The globally averaged tropospheric hydroxyl and ozone concentrations are $[\bullet OH]$ and $[O_3]$. We have calculated (in agreement with some experimental data) that rate constants for reaction with hydroxyl free radicals increase by a factor of approximately 200 for addition of an ether linkage adjacent to a hydrogen atom. This gives atmospheric lifetimes as short as 0.3 years for some hydrofluoroethers (HFE). Replacement of a fluorine with a bromine will reduce the atmospheric lifetime by about a factor of 10. Thus brominated HFEs should have atmospheric lifetimes as short as 11 days. Similar results hold for brominated hydrofluoroamines. Carbonyl compounds comprise the only family among those being investigated where there is significant absorption and photodissociation in the troposphere (i.e., absorption for $\lambda = 299$ nm to 700 nm). Excluded in this statement is the photodissociation inherent in all of these materials due to the presence of bromine. Unsaturated compounds (primarily alkenes and aromatics) have very short lifetimes (on the order of days or less) due to interaction with tropospheric $\bullet OH$ and O_3.

G.   CONCLUSIONS

The tropodegradable halocarbon families that exhibit halon replacement potential, and which are being emphasized in this effort, are hydrobromofluoroethers (HBFE), hydrobromo-fluoroamines (HBFA), fluorobromo unsaturated compounds (alkenes and aromatics), and bromofluorocarbonyl compounds. Most of the materials are highly fluorinated (to decrease flammability and hepatotoxicity), but in many cases are not completely fluorinated.

H.   RECOMMENDATIONS

Additional information is needed in the following areas for tropodegradable compounds that show promise as halon replacements: (1) synthetic routes and manufacturability, (2) detailed toxicology, (3) emission characterization, and (4) extinguishment mechanisms and structural features enhancing extinguishment. The first two items should be addressed in the next stage of work.

PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the Infrastructure Technology Section of Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates (ARA), Inc., Tyndall Air Force Base, Florida, under SETA Task 3.12, Air Force Contract S-5000.31, NMERI Number 8-32540. This document provides a technology review tropodegradable compounds as potential streaming agents for replacement of Halon 1211.

The Start Date for the overall Advanced Streaming Agent Program was 9 August 1995, and the End Date is 30 April 1996. The WL/FIVCF Project Officer is Major Robert A. Tetla, the ARA Project Officer is Michael A. Rochefort, and the NMERI Principal Investigator is Robert E. Tapscott.

NMERI 96/4/32540

SECTION I

INTRODUCTION

A.   OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

This document is Volume IV of the final report and provides an assessment of tropodegradable halocarbons as potential substitutes for replacement of Halon 1211 in streaming applications. The five volumes of the final report are listed below:

Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/1/32540

Patterson, R. A., Gobeli, G. W., Brabson, G. D., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume II: Metal Compounds*, WL-TR-96-XX, Vol. 2 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/3/32540

Kaizerman, J. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume III: Phosphorus Compounds*, WL-TR-96-XX, Vol. 3 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/5/32540

Heinonen, E. W., Lifke, J. L., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons*, WL-TR-96-XX, Vol. 4 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/4/32540

1

Lifke, J. L., Moore, T. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests*, WL-TR-96-XX, Vol. 5 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/2/32540

B.   BACKGROUND

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of the fire and explosion protection agents Halon 1211 and Halon 1301 was phased out in the United States at the end of 1993. To date, no environmentally acceptable halon substitute that is equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified.

Halocarbons as replacements for halons have been well studied, and it is unlikely that new, highly effective, halon replacements will be identified among the typical non-iodinated haloalkanes. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs (for an overview, see Reference 1). The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide (CF_3I), which is as effective as the existing halons. However, the toxicity of the iodides restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the typical haloalkanes.

Recent work has identified several potential non-halocarbon (References 2 and 3) and low-atmospheric-lifetime halocarbon (Reference 4) substitutes for halon fire extinguishants. In particular, work by the Advanced Agent Working Group, AAWG, which includes U.S. Air Force (USAF) and U.S. Army participation, has shown that the most promising of the non-halocarbon compounds are phosphorus compounds (particularly, phosphorus nitrides, which include the phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds (Reference 5). The AAWG work, which emphasizes chemical options for total-flood Halon-

1301 applications, and work by the USAF also show that tropodegradable halocarbons, which contain features that induce short atmospheric lifetimes, exhibit high promise.

C.   SCOPE

Four separate tasks are included in the overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal complexes, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

Task 2: Synthesis of New Compounds. Samples of the most promising of these materials based on expected toxicity, availability/manufacturability, and environmental characteristics are to be prepared or obtained.

Task 3: Laboratory Evaluations. Laboratory-scale evaluations of fire extinguishment by these materials are to be performed. Preliminary analyses of global environmental impact, toxicity evaluations, and manufacturing/synthesis assessment of the candidates identified for follow-on testing are to be conducted.

Task 4: Final Report. The information obtained is to be used to prepare a final report detailing the work performed, the results obtained, and conclusions. The report will make recommendations for continuation of large-scale testing with the most promising agents.

D.   APPROACH

With the exception of the iodides, which possess fire extinguishment performance combined with low atmospheric lifetimes, all of the compounds discussed in this report contain bromine. Introduction of bromine into compounds with very short atmospheric lifetimes allows the production of candidates with very low Ozone Depletion Potentials (ODP), while maintaining fire extinguishment effectiveness. Since the target for these materials is an ODP less than that of the HCFCs, and since these compounds are likely to have no commercial application

3

other than as halon replacements (unlike the HCFCs), the chances for regulatory restrictions are greatly reduced.

Parameters determining global environmental impacts have been reviewed and tropodegradability is defined. The mechanisms for removal from the troposphere are discussed, and chemical features that induce susceptibility to the most effective removal mechanisms have been determined. The chemical, physical, and toxicological characteristics are assessed for each halocarbon family identified. Limited laboratory testing has been carried out on selected halocarbons belonging to various families of tropodegradable chemicals.

SECTION II

GLOBAL ENVIRONMENTAL CHARACTERISTICS

Since environmental properties are of particular importance in defining tropodegradability, the following contains an overview of the environmental properties of particular interest (Reference 6).

A.   ATMOSPHERIC REGIONS

The concentration of ozone in the earth's atmosphere increases with altitude until it reaches a maximum near 50 km (Figure 1). In part due to this variation in ozone, the temperature of the atmosphere varies with altitude. Near the earth, atmospheric temperature decreases with altitude until heating due to absorption of sunlight by the ozone causes a reversal of the temperature gradient around 12 km at a boundary termed the "tropopause." The temperature continues to increase until the ozone concentration is sufficiently small that heating can no longer offset the "normal" decrease in temperature. At this boundary, the "mesopause," the temperature once more begins to decrease. Note that the locations of these boundaries depend on the latitude, and the boundaries are not sharply defined.

Based on the locations of the atmospheric temperature changes, the earth's atmosphere can be divided into regions (Figure 2). The most important of these for the topics of interest here are the troposphere, the region nearest the earth's surface, and the stratosphere, the region containing most of the protective ozone layer.
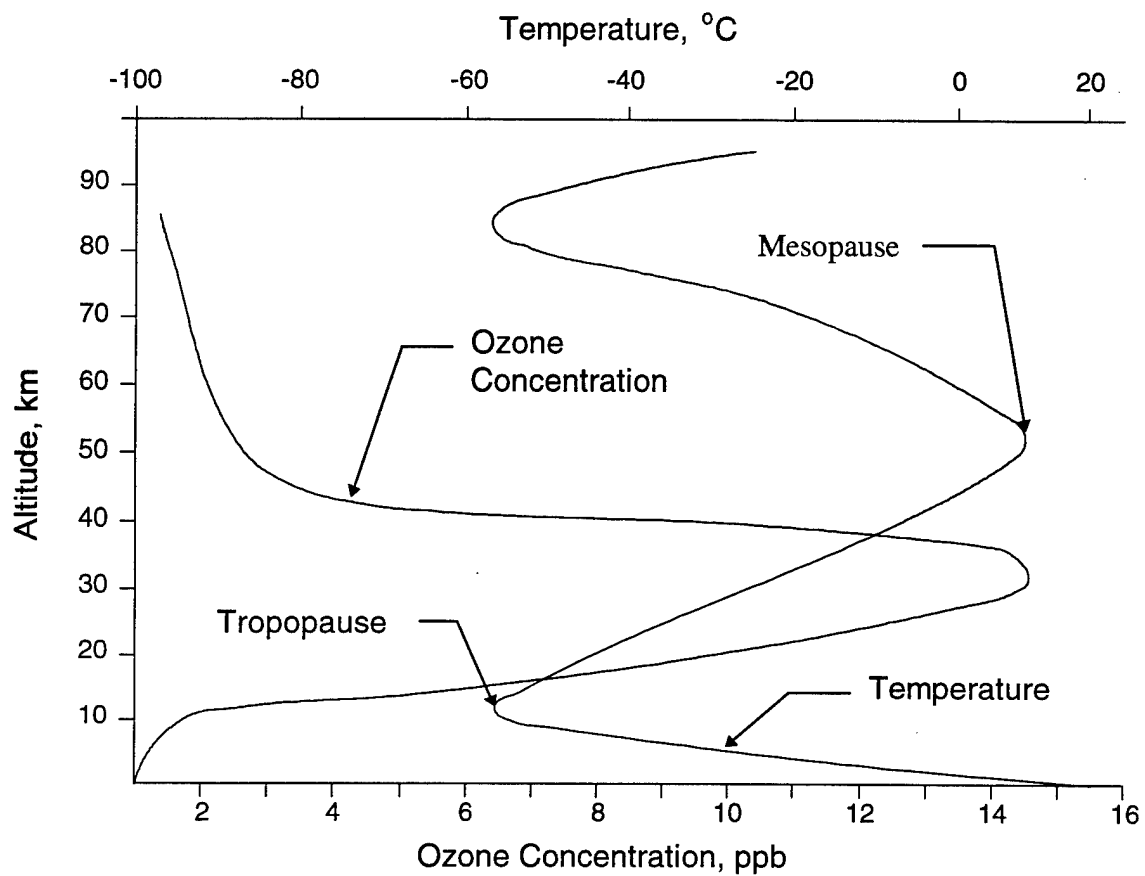
Figure 1. Atmospheric Temperature and Ozone Concentration as a Function of Altitude.

Mesosphere
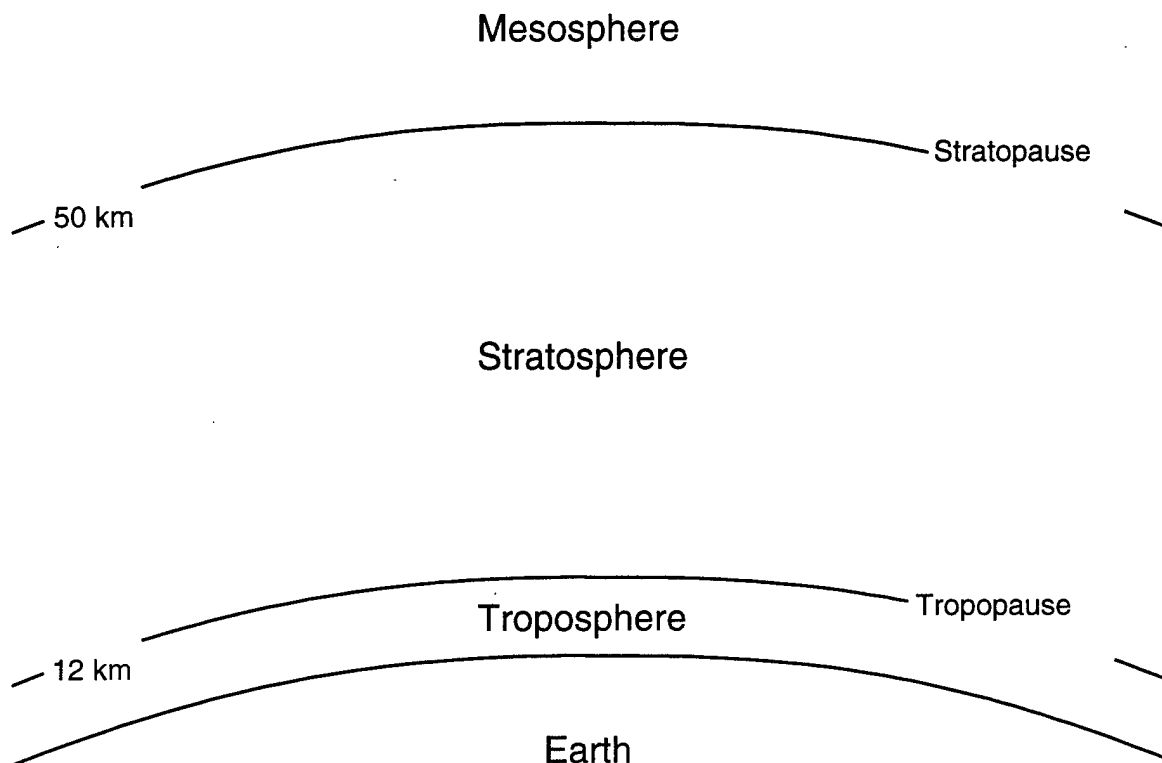
Figure 2. Atmospheric Regions.

B.   OZONE DEPLETION POTENTIAL

ODPs are the calculated ozone depletions per unit mass of material released relative to a standard, normally CFC-11 (trichlorofluoromethane, CCl_3F).[*] It should be noted that ODPs are calculated; they cannot be measured. The calculations require the generation of hypothetical atmospheric layers or cells for which material balances are calculated by computer (Figure 3). The material balances are based on transport of material into and out of the cells allowing for

---

[*]See Appendix A for a review of halocarbon numbers such as "CFC-11" and nomenclature.

7

material formed in a cell (sources) and material removed or modified to give other compounds (sinks).

Calculations of ODPs require time horizons (see below); however, steady-state calculations are often used. Although ODPs vary somewhat depending on the calculation method, it is believed that relative values for compounds containing the same ozone-depleting element are relatively reliable. Thus, halocarbons that contain only chlorine and fluorine (in addition to carbon and, possibly, hydrogen) can be compared to CFC-11. It is well established that bromine is much more damaging to ozone than is chlorine on a per atom basis. Exactly how much more, however, is not precisely known and lends some uncertainty to the ODPs of bromocarbons. An excellent nontechnical historical overview is contained in Reference 7.
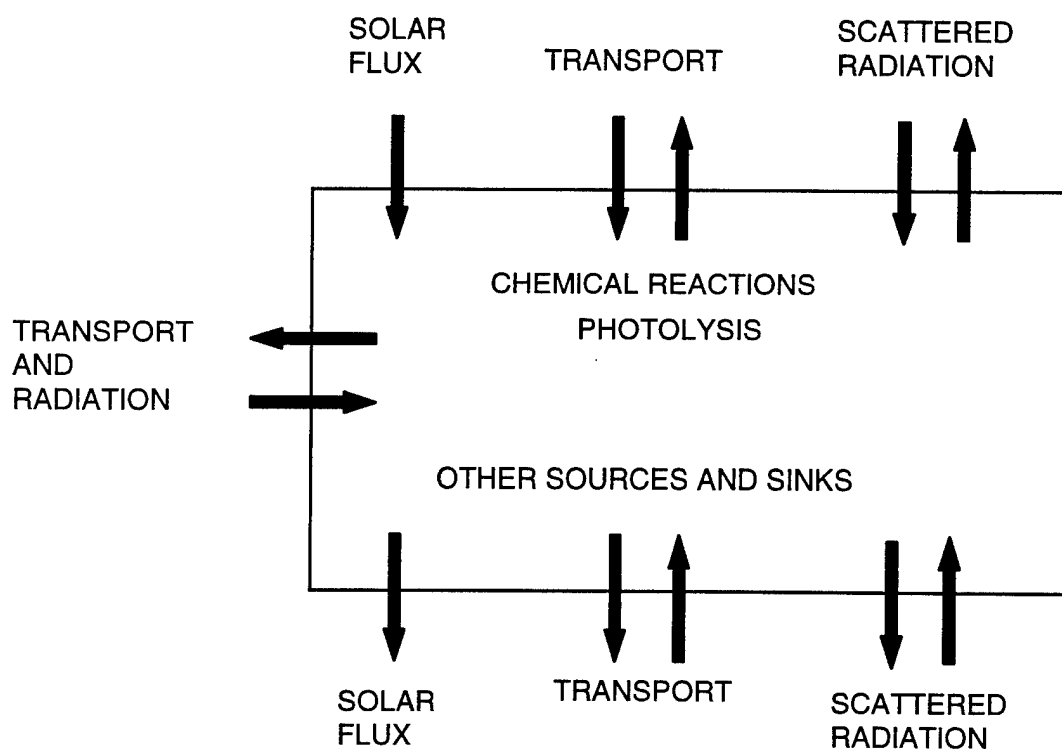
Figure 3. An Atmospheric Cell with Parameters Affecting Mass and Energy Balances.

C. ATMOSPHERIC LIFETIME

Atmospheric lifetimes are generally modeled as "e-folding" lifetimes ($t_{1/e}$). The gas concentration decays exponentially following Equation 1.*

$$C_t = C_o e^{t/t_{1/e}} \qquad [1]$$

where C_o is the initial concentration, C_t is the concentration at any time t, and $t_{1/e}$ is the atmospheric lifetime. After one lifetime ($t_{1/e}$), the gas concentration drops to $1/e$ (approximately 0.369) of its initial value. Note that Equation 1 predicts that the concentration will never reach zero, although it can approach it very closely. For example, after only five lifetimes, the concentration drops to 0.0067 of its initial value.

Occasionally, the time required for a concentration to reach one-half of its initial value is used in place of the atmospheric lifetime. These times are denoted as $t_{1/2}$ defined by Equation 2, where ln 2 is the logarithm of 2 to the base e (i.e., 0.693).

$$t_{1/2} = (t_{1/e})(\ln 2) \qquad [2]$$

D. GLOBAL WARMING POTENTIAL

The Global Warming Potential (GWP) is the change in radiative forcing resulting from the emission of 1 kg of a chemical relative to the radiative forcing resulting from the emission of 1 kg of a reference gas. In the past, CFC-11 was often used as the reference; however, carbon dioxide is now typically used. The GWP depends on three variables: (1) the integrated infrared (IR) radiation absorption spectrum band strength; (2) the location of the IR spectral absorption bands; and (3) the lifetime of the gas. The calculations are similar to those carried out for ODP except that energy balances (rather than mass balances) based on radiation input, output, and absorption are the focal point (Figure 3). It is important to note that the GWP can vary significantly depending on the time period used for the comparison of the radiative forcing of the

---

*Throughout this report, equation numbers are inserted in brackets, [], and chemical reaction numbers are placed in parentheses, ().

chemical relative to that of the reference. The time period used to calculate the GWP is termed the "time horizon" and is primarily a policy decision. Time horizons of 100 and 500 years are often used in calculated GWP values; however, other time horizons may be more appropriate. GWPs with longer time periods are believed to be more inaccurate that those with shorter time periods (Reference 8).

E.   TROPODEGRADABLE HALOCARBONS

In this report, the term "tropodegradable" is used for any halocarbon with an atmospheric lifetime on the order of days or weeks. This definition is used since it is known that chlorine-containing compounds such as the HCFCs, which have atmospheric lifetimes of months or longer, are being regulated under the Montreal Protocol. Since precise atmospheric lifetimes are not known for most tropodegradable chemicals, a more precise definition of tropodegradability is not useful.

Tropodegradable halocarbons help solve three environmental problems—atmospheric lifetime, global warming, and ozone depletion. In general, GWPs and ODPs increase with atmospheric lifetime. This can be seen in an examination of the atmospheric lifetimes and ODPs for HCFCs and CFCs shown in Table 1 (References 9 and 10). Because the compounds contain varying amounts of chlorine, simple plots of ODP as a function of atmospheric lifetime show no clear trend (Figures 4 and 5). When the ODPs are divided by the number of chlorine atoms in a molecule, however, the trend becomes obvious (Figures 6 and 7).

TABLE 1. ATMOSPHERIC LIFETIMES AND ODP VALUES FOR COMMON HCFCs AND CFCs.

Halocarbon number	IUPAC name	Formula	Lifetime, years	ODP
HCFC-141b	1,1-dichloro-1-fluoroethane	CH_3CCl_2F	9.4	0.1
HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane	$CHClFCF_3$	5.9	0.03
HCFC-123	2,2-dichloro-1,1,1-trifluoroethane	$CHCl_2CF_3$	1.4	0.014
HCFC-225ca	3,3-dichloro-1,1,1,2,2-pentafluoropropane	$CF_3CF_2CHCl_2$	2.5	0.02
HCFC-225cb	1,3-dichloro-1,1,2,2,3-pentafluoropropane	$CClF_2CF_2CHClF$	6.6	0.02
HCFC-22	chlorodifluoromethane	$CHClF_2$	13.3	0.04
HCFC-142b	1-chloro-1,1-difluoroethane	CH_3CClF_2	19.5	0.05
CFC-11	trichlorofluoromethane	CCl_3F	50	1
CFC-12	dichlorodifluoromethane	CCl_2F_2	102	0.82
CFC-13	chlorotrifluoromethane	$CClF_3$	640	1
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane	CCl_2FCClF_2	85	0.9
CFC-114	1,2-dichloro-1,1,2,2-tetrafluoroethane	$CClF_2CClF_2$	300	0.85
CFC-115	chloropentafluoroethane	$CClF_2CF_3$	1700	0.4
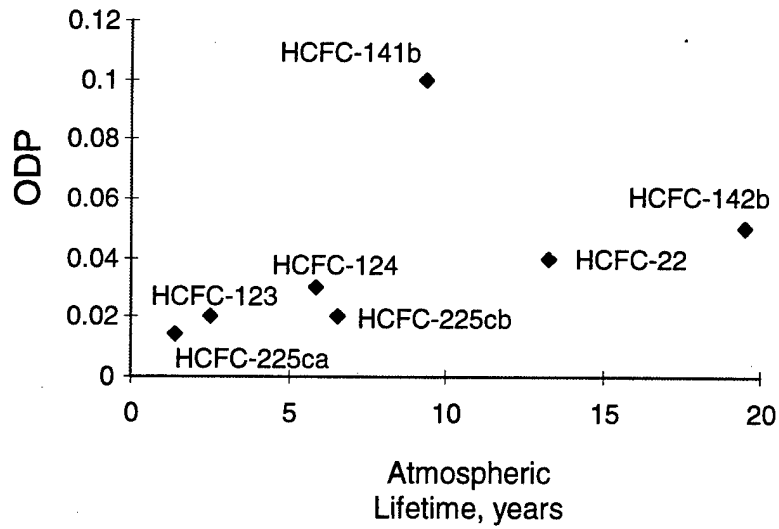
Figure 4. ODP as a Function of Atmospheric Lifetime for HCFCs.
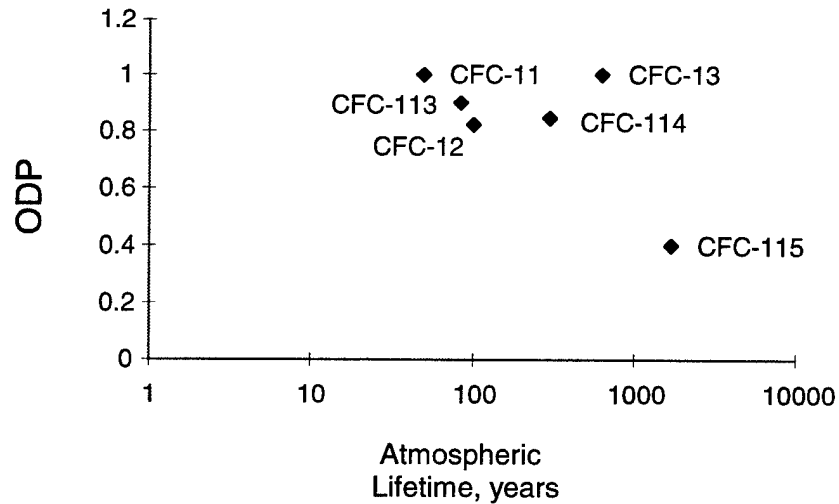
Figure 5. ODP as a Function of Atmospheric Lifetime for CFCs.
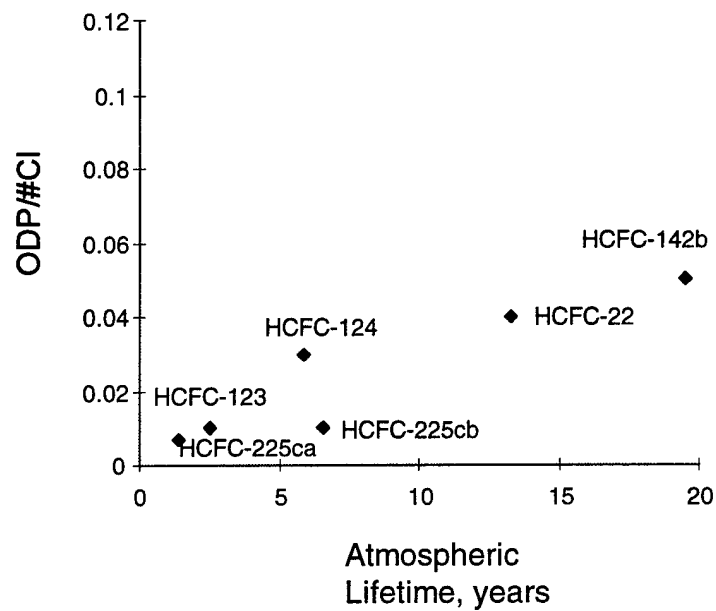
Figure 6. ODP Divided by Number of Chlorine Atoms as a
Function of Atmospheric Lifetime for HCFCs.
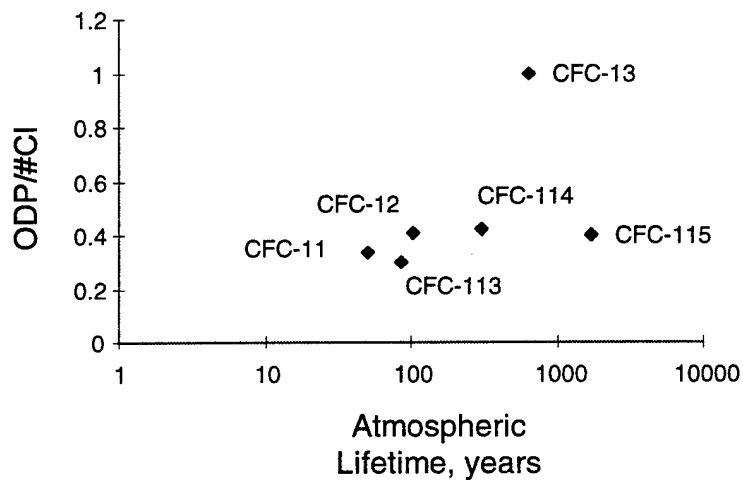
Figure 7. ODP Divided by Number of Chlorine Atoms as a
Function of Atmospheric Lifetime for CFCs.

SECTION III
TROPOSPHERIC REMOVAL MECHANISMS

A. INTRODUCTION

Four primary processes exist for removal of organic molecules from the troposphere: (1) reaction with atmospheric hydroxyl free radicals; (2) photolysis; (3) physical removal; and (4) reaction with tropospheric ozone. Not considered in this report are thermal and other processes that may remove highly reactive chemicals such as peroxides (References 11 and 12), epoxides, and organic nitrates, since all of these highly reactive species are likely to have toxicological and stability characteristics making them unsuitable for consideration as candidates for replacement of halons. Compounds can also be degraded by reaction with a number of other atmospheric species including oxygen atoms in the ^3P and ^1D electronic states (e.g., Reaction 1), NO_x, nitric acid, and peroxy species. Such reactions are relatively minor tropospheric degradation processes for chemicals discussed in this report, however, and will not be considered further (Reference 13).

$$RH + \bullet O(^1D) \rightarrow \bullet R + \bullet OH \tag{1}$$

A rate constant can be assigned to each of these processes—k_{OH} for reaction with hydroxyl free radicals, $k_{physical}$ for physical removal, k_{photo} for photolysis, and k_{O3} for reaction with tropospheric ozone. The units used throughout this report are cm^3/molecule-s for k_{OH} and k_{O3} and s^{-1} for $k_{physical}$ and k_{photo}. The rate constants vary not only with the chemical being removed from the troposphere, but are also a function of the atmospheric position (which determines the hydroxyl free radical concentration, temperature, and solar flux). As an approximation, one can use, for all but k_{photo}, the globally averaged rate constants. An overall pseudo first-order rate constant k_1 can be written, where $k_1 = k_{OH}[\bullet OH] + k_{physical} + k_{photo} + k_{O3}[O_3]$, $[\bullet OH]$ is a globally averaged tropospheric hydroxyl free radical concentration (9.7×10^5 molecules/cm^3 [Reference 14]), and $[O_3]$ is the globally averaged tropospheric ozone

14

concentration (5.0×10^{11} molecules/cm^3 [Reference 15]).* The rate constant gives the time rate of change of the atmospheric concentration of a compound C, e.g., d[C]/dt, where brackets indicate concentration, d is a differential, and t is time (Equation 3). The atmospheric lifetime ($t_{1/e}$) is then given by Equation 4.

$$\frac{d[C]}{dt} = -k_1[C] \qquad [3]$$

$$t_{1/e} = 1/k_1 \qquad [4]$$

Wuebbles and Connell have presented a simplified screening methodology to estimate tropospheric lifetimes for a variety of halogenated chemicals (Reference 15), and this methodology will be applied in this report for some estimations.

B.   REACTION WITH HYDROXYL FREE RADICALS

For the compounds of interest here, the hydroxyl free radicals can abstract a hydrogen atom and/or add to an unsaturated molecule to yield products (Reaction 2). The effectiveness of hydroxyl radical reactions in removing compounds from the atmosphere depends on the reaction rate constant (k_{OH}) and the atmospheric concentration of hydroxyl free radicals (•OH) (Reference 16). The rate constant k_{OH} gives the time rate of change of the concentration of a compound C in the atmosphere due to reaction with •OH only (Equation 5) and can be written as the sum of the rate constants for hydrogen atoms abstraction (k_{OH}^1) and for hydroxyl addition to an unsaturated compound (k_{OH}^2). The atmospheric half-life of a chemical for which the sole removal mechanism is reaction with hydroxyl free radicals is given by Equation 6 (Reference 17). Here, the hydroxyl radical concentration is taken to be constant. Equation 6 can be rewritten to yield the atmospheric lifetime (i.e., the e-folding lifetime) to give Equation 7. One can use Equation 7 to estimate lifetimes by assuming pseudo first-order behavior and using the globally averaged hydroxyl free radical concentration of 9.7×10^5 molecules/cm^3

---

*Pseudo first-order behavior assumes that the concentration of the hydroxyl free radical or tropospheric ozone remains constant and can be "averaged" into the second-order rate constants to give a pseudo first-order rate constant (k_1).

15

(Reference 14). Large numbers of rate constants for reactions of hydroxyl free radicals with organic compounds are available (References 18 and 19).

$$C + \bullet OH \xrightarrow{k_{OH}} products \tag{2}$$

$$\frac{d[C]}{dt} = -k_{OH}[C][\bullet OH] \tag{5}$$

$$t_{1/2} = \frac{\ln 2}{k_{OH}[\bullet OH]} \tag{6}$$

$$t_{1/e} = \frac{1}{k_{OH}[\bullet OH]} \tag{7}$$

1. Hydrogen Atom Abstraction

All compounds containing a hydrogen atom (e.g., hydrocarbons, HFCs, and HCFCs) are subject to reaction with tropospheric hydroxyl free radicals as shown in Reaction 3, where R represents any organic or halogenated organic group (Reference 20). Here, Equation 5 can be rewritten as Equation 8.

$$RH + \bullet OH \xrightarrow{k_{OH}} \bullet R + H_2O \tag{3}$$

$$\frac{d[RH]}{dt} = -k_{OH}[RH][\bullet OH] \tag{8}$$

CFCs have no hydrogen atoms and undergo little, if any, reaction with •OH free radicals while passing through the atmosphere. They only decompose upon reaching the stratosphere, where photolysis can occur. The HCFCs and HFCs, on the other hand, do undergo hydrogen atom abstraction by hydroxyl free radicals in the troposphere, though this may not be sufficiently rapid to give the near-zero ODPs desired for the HCFCs or the very small GWPs desired for the HFCs and HCFCs.

The organic free radical •R formed in Reaction 3 rapidly reacts with diatomic oxygen (O_2) to form a peroxy radical (ROO•), which further reacts to give a series of products. In most cases, these final products are rapidly removed by physical processes so that they do not contribute significantly to ozone depletion or global warming.

Reaction 3 is too inefficient, for most saturated haloalkanes, to be considered as giving tropodegradable compounds as defined in this report; i.e., compounds with a rapid degradation giving atmospheric lifetimes on the order of days or weeks. This can be seen in the atmospheric lifetimes of 0.4 to 19.5 years for common HCFCs and from 1.5 to 250 years for common HFCs (Reference 10). Hydrogen atom abstraction by atmospheric hydroxyl free radicals is the primary tropospheric removal process for both HCFCs and HFCs.

Note, however, that Reaction 3 is more rapid for many compounds other than the normal haloalkanes. It has been found that the activation energy for hydrogen atom abstraction decreases (as expected) with decreasing dissociation energy of the C-H bond (References 21 and 22). Thus, as the bond dissociation energy decreases, the reaction rate with hydroxyl free radicals increases. For example, for a wide range of compounds, replacement of either a fluorine atom or a hydrogen atom by an oxygen atom alpha to a CH group decreases the bond dissociation energy and increases the reaction rate (decreasing the atmospheric lifetime). Thus, aldehydes, (RC(O)H) react sufficiently rapidly (Reaction 4) that they have atmospheric lifetimes on the order of days (References 23 and 24). A similar phenomenon is seen for alcohols. Beta substitution generally has a much lower substituent effect on bond dissociation energies (Reference 25).

$$RC(O)H + \bullet OH \rightarrow \bullet CR(O) + H_2O \tag{4}$$

2.   Addition of Hydroxyl Free Radicals to Unsaturated Organics

Unsaturated organics are any compounds containing multiple carbon to carbon bonds. Addition of •OH free radicals to unsaturated chemicals is a highly effective removal process. For alkenes, the hydroxyl radical adds to give a highly energetic product radical (Reaction 5, where the asterisk indicates an activated species.). If it does not lose another group,

17

the energetic product can then either revert back to reactants, or it can be stabilized by collision with another molecule (M), which can carry off the excess energy (Reaction 6). The reverse reaction is probably not important below 100 °C, higher than temperatures found in the troposphere (Figure 1). Hydroxyl free radicals can also add to a triple bond (Reaction 7) and to aromatics. Due to potential manufacturing difficulties and stability problems, alkynes (compounds containing triple bonds) are not considered as halon replacement candidates; however, aromatic compounds are.

$$\ce{>C=C< + \cdot OH -> -\underset{|}{\overset{OH}{C}}-\overset{*}{C}\cdot<} \tag{5}$$

$$\ce{>C=C< + \cdot OH <- -\underset{|}{\overset{OH}{C}}-\overset{*}{C}\cdot< + M -> -\underset{|}{\overset{OH}{C}}-\overset{}{C}\cdot< + M^*} \tag{6}$$

$$\ce{-C\equiv C- + \cdot OH -> \overset{HO}{>}C=\overset{*}{C}\cdot} \tag{7}$$
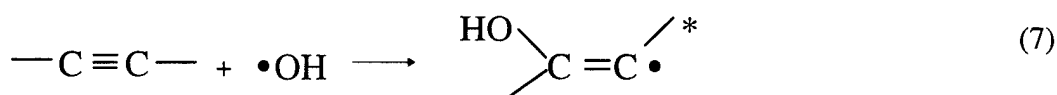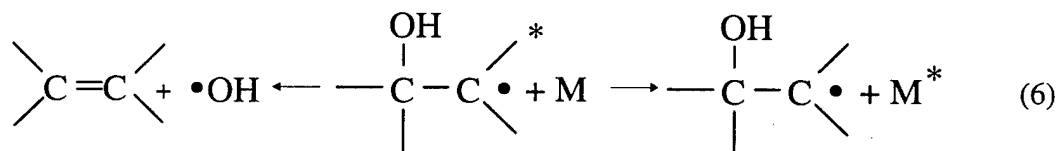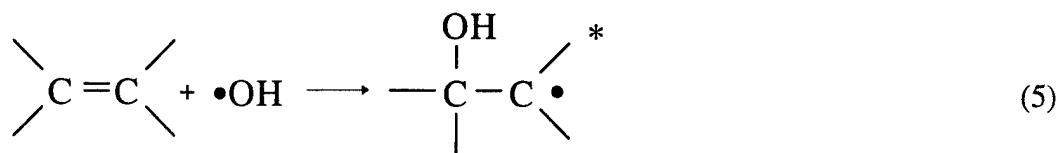
C. PHOTOLYSIS

Photolysis (also called photodegradation and photolytic decomposition) requires absorption of electromagnetic radiation with resulting molecular decomposition. The photodecomposition reactions have the form shown in Reaction 8, where the products are fragments of the original reactant molecule. Planck's constant (h) multiplied by the frequency of the electromagnetic radiation (ν) gives the energy of a single photon of radiation with that frequency, and "hν" is often used as a symbol for a photon in a chemical equation (e.g., Reaction 8). As the frequency of the electromagnetic radiation increases and the wavelength (λ) decreases, the energy per photon increases. Thus, shorter wavelength electromagnetic radiation, such as ultraviolet (UV), is usually more effective in effecting photodegradation than is longer

18

wavelength radiation, such as visible and infrared (IR). Photolysis of a molecule depends on two parameters, the absorption cross section (σ)(which determines how much of the available light is absorbed) and the quantum yield (φ) (the fraction of the absorbed photons that affects photolysis). If every photon absorbed produces a reaction, $\varphi = 1$.

$$\text{Reactant} + h\nu \rightarrow \text{Products} \tag{8}$$

Most organic compounds exhibit decreasing absorption cross sections as the radiation wavelength increases (at least for the ultraviolet and visible spectral regions). Since much of the lower wavelength, higher energy solar radiation is removed by stratospheric ozone before sunlight reaches the troposphere (particularly UV-B radiation, with wavelengths between 180 and 320 nanometers [Figure 8]), many molecules do not encounter electromagnetic radiation of a sufficiently short wavelength for absorption until they reach the stratosphere. For example, the CFCs (chlorofluorocarbons) absorb little if any solar radiation required for photolytic decomposition as they pass through the troposphere. On the other hand, in the stratosphere, where short wavelength UV radiation is intense, the CFCs photodecompose to release chlorine.
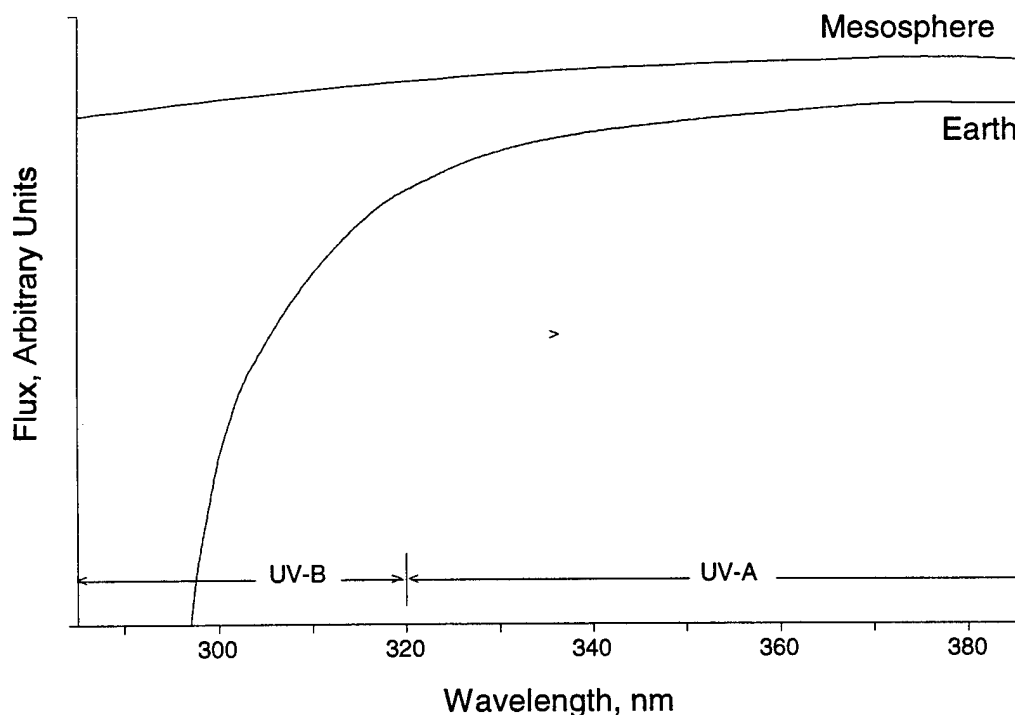
Figure 8. Radiative Flux as a Function of Wavelength.

19

Photodissociation in the troposphere requires that a compound absorb radiation in the wavelength range from 299 nm to 700 nm (Reference 15). The photodissociation rate constant k_{photo} is determined by Equation 9, where $\sigma(\lambda)$ is the absorption cross section as a function of the wavelength λ, $I(\lambda)$ is the solar intensity as a function of λ, and $\varphi(\lambda)$ is the photodissociation quantum yield. Thus, a chemical compound has two characteristics that determine the importance of photolysis: (1) the absorption cross section (how well it absorbs electromagnetic radiation encountered in the troposphere) and (2) the quantum yield. Both of these are a function of the electromagnetic radiation wavelength. The atmospheric lifetime for photodissociation only is then given by Equation 10.

$$k_{photo} = \int_{290nm}^{700nm} \sigma(\lambda)I(\lambda)\varphi(\lambda)d\lambda \qquad [9]$$

$$t_{1/e} = 1/k_{photo} \qquad [10]$$

In general, halocarbons require one of the groups shown in Figure 9 to be present for there to be significant absorption and photodissociation in the troposphere (i.e., absorption for λ = 299 nm to 700 nm). Only the ketones and iodides are of major interest here; however, compounds with conjugated double bonds (i.e., double bonds that allow some delocalization of the π electron cloud) and compounds containing a double bond conjugated to an aromatic could form the basis for more "exotic" fire suppressants. In addition, photolysis of bromine compounds will assist in lowering the atmospheric lifetimes for bromine-containing compounds (those proposed herein).

| Carbonyl, R ≠ OH or OR | Conjugated Double Bonds | Double Bond Conjugated to Aromatic |
| Polynuclear Aromatic | Nitro-Substituted Benzene | Bromine or Iodine |
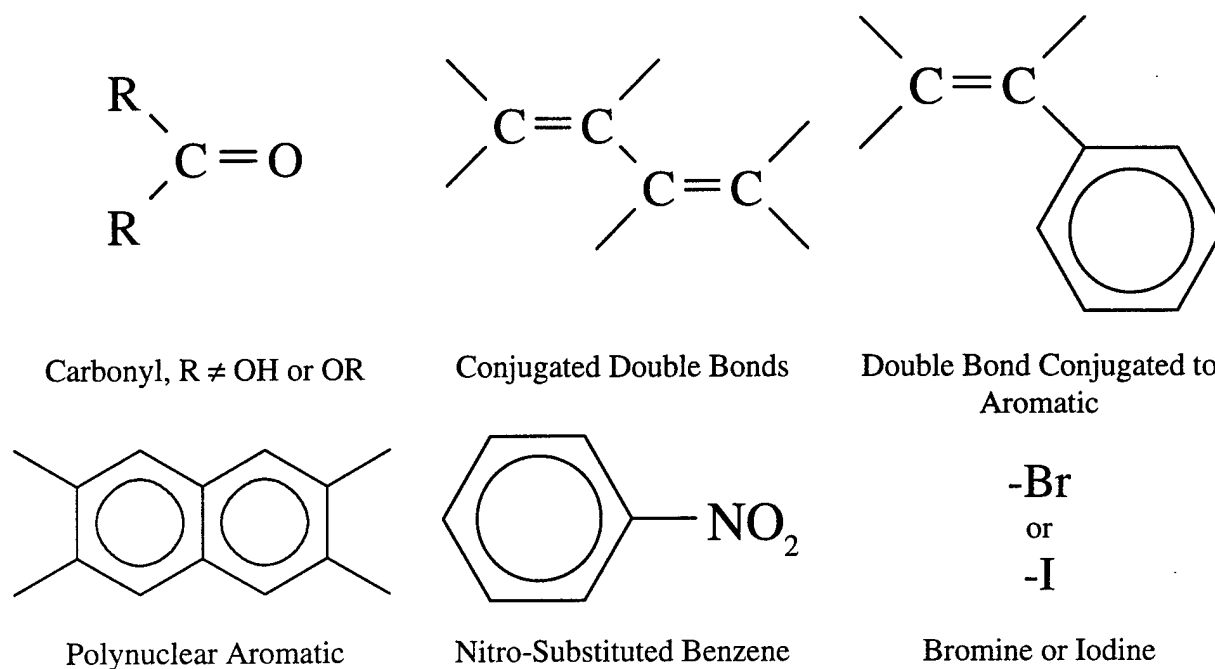
Figure 9. Groups Required for Significant Tropospheric Photodissociation.

D.   PHYSICAL REMOVAL PROCESSES

Physical removal processes include (1) rainout (absorption by water droplets), (2) aerosol scavenging, and (3) solution into oceans (Reference 15). The science of physical removal lags far behind that of the other tropospheric removal processes, and much is qualitative.

1.   Rainout

Rainout is believed to be a highly effective tropospheric removal mechanism for highly polar compounds such as hydrogen halides (HX, where X represents a halogen atom) and carbonyl halides ($O=CX_2$). Absorption by water droplets, "rainout," often occurs with concurrent hydrolysis (Reference 26). For example, the carbonyl halides undergo hydrolysis following absorption to form carbon dioxide and hydrogen halides (Reaction 9). Effective hydrolysis requires a heterogeneous reaction involving water droplets, since homogeneous hydrolysis is very slow (Reference 27). For highly hydrophilic compounds such as nitric acid (HNO_3), the global time constant for rainout is about 7 days (Reference 28).

$$O=CX_2 + H_2O \rightarrow CO_2 + 2HX \tag{9}$$

As the polarity of a compound decreases, physical removal by water absorption becomes less and less effective. For the relatively nonpolar CFCs, HCFCs, HFCs, and PFCs, tropospheric rainout is essentially nonexistent.

Equation 11 has been proposed to estimate the atmospheric lifetime for rainout (Reference 29). Here, α is the solubility coefficient defined by Equation 12. The saturation vapor density is the density of vapor in equilibrium with liquid at a particular temperature (which can be taken as 298 K). Rainout could be significant for highly water-soluble compounds (large values of α) such as alcohols, amines, and carbonyl compounds (esters, carboxylic acids, aldehydes, ketones); however, substitution with fluorine will greatly decrease the solubility and, consequently, the rainout. For example, due to the very low polarity, perfluoroamines such as tris(trifluoromethyl)amine ($N(CF_3)_3$) are likely to have little if any significant removal by rainout.

$$t_{1/e} \approx \frac{8000}{\alpha} \text{ years} \tag{11}$$

$$\alpha = \frac{\text{solubility (g/L)}}{\text{saturation vapor density (g/L)}} \tag{12}$$

2.   Aerosol Scavenging

Aerosol scavenging involves adsorption of a chemical onto solid particulates. Equation 13 has been advanced to predict the atmospheric lifetime due to aerosol scavenging (Reference 29). Here, P_{vap} is the vapor pressure of a compound in Torr at 298 K. For adequate tropodegradability of the compounds of interest in this project, the atmospheric lifetime should be less than one month (2.625×10^6 seconds). Solving for the P_{vap} required to achieve this, one obtains $P_{vap} = 1.625 \times 10^{-7}$ Torr. This vapor pressure is far too low for any halocarbon sufficiently volatile to be considered as a multidimensional fire extinguishant, and, therefore, aerosol scavenging will not be considered further.

$$t_{1/e} = 10^6(10^7 P_{vap} + 1) \text{ seconds} \tag{13}$$

3.   Solution Into Oceans

The lower limit for the tropospheric lifetime due to absorption (solution) into oceans can be estimated by Equation 14 (Reference 30). Here β is the (ocean) water solubility of a gas in moles/m^3-atm (essentially, a Henry's law constant), D is the molecular diffusivity of a gas in water in m^2/year (Reference 31), and z is the film thickness in the classical stagnant film model for gas exchange. The film thickness is approximately 30 x 10^{-6} m, and an upper limit on diffusivity at 298 K (giving a lower limit on the lifetime) is approximately 6 x 10^{-5} cm^2/sec (1.9 x 10^{-1} m^2/year) (Reference 30). This gives an upper limit on D/z of 6 x 10^3 m/yr and a lifetime with a lower bound given by Equation 15. This is a lower bound to the atmospheric lifetime, which is not only because a particularly large value was placed on D/z, but also because of release from the ocean back into the atmosphere, a process not taken into account in this approximation. To obtain a lifetime of less than 1 month by this process, one needs compounds with a water solubility greater than 60 moles/m^3-atm. This is a rather large solubility. For example, the solubility of carbon dioxide, a highly water soluble gas, is only about 40 moles/m^3-atm (Reference 30). There is a possibility that ocean solubility could play some role in removal of carbonyl compounds and alcohols, but the contribution is likely to be small.

$$t_{1/e} = \frac{3 \times 10^5}{\beta D/z} \qquad\qquad [14]$$

$$t_{1/e} \geq \frac{50}{\beta} \text{ years} \qquad\qquad [15]$$

E.   REACTION WITH TROPOSPHERIC OZONE

The only chemicals exhibiting rapid reaction with tropospheric ozone are the alkenes. The mechanisms of these reactions are not well understood, and the potential for reaction of highly fluorinated alkenes with tropospheric ozone is uncertain. For a globally averaged tropospheric ozone concentration of $[O_3] = 5.0 \times 10^{11}$ molecules/cm^3 and with a maximum rate constant of 2 x 10^{-16} cm^3/molecule-s (Reference 15), one can calculate a first-order reaction rate constant of $k_1 = (k_{O3})[O_3] = 1 \times 10^{-4}$. The determination of this rate constant allows a calculation

23

for the atmospheric lifetime of $t_{1/e} = 1/k_1 = 10^4$ seconds or less than one day. Thus, removal by tropospheric ozone could be significant for alkenes. This is discussed further in the section on alkenes.

F.   OVERVIEW OF REMOVAL PROCESSES

Most compounds are removed by a variety of mechanisms. For example, the various removal mechanisms for the halons are shown in Figure 10.[*] Essentially no tropospheric removal is found for Halon 1301. This highly stable material is only destroyed in the stratosphere. Halon 1201 is the only compound among those shown that contains hydrogen and is, therefore, the only compound that undergoes reaction with hydroxyl free radicals. Photolysis is a relatively important removal process for Halons 1211, 2402, and, in particular, 1202. The last compound contains two bromine atoms attached to the same carbon atom (it is a "geminal dibromide"). Such compounds absorb light readily and are, therefore, highly subject to photolysis. None of these relatively nonpolar organic compounds exhibits any significant tendency for removal by physical processes.

Table 2 lists the various mechanisms and the families that are likely to have significantly decreased tropospheric lifetimes due to each mechanism.

---

[*]Connell, P. S., and Wuebbles, D. J., "Ozone Depletion Potential, Halons, and Halon Alternatives," presented at the NMERI Halon Alternatives Program Review, Albuquerque, New Mexico, 23-24 January 1991.

24
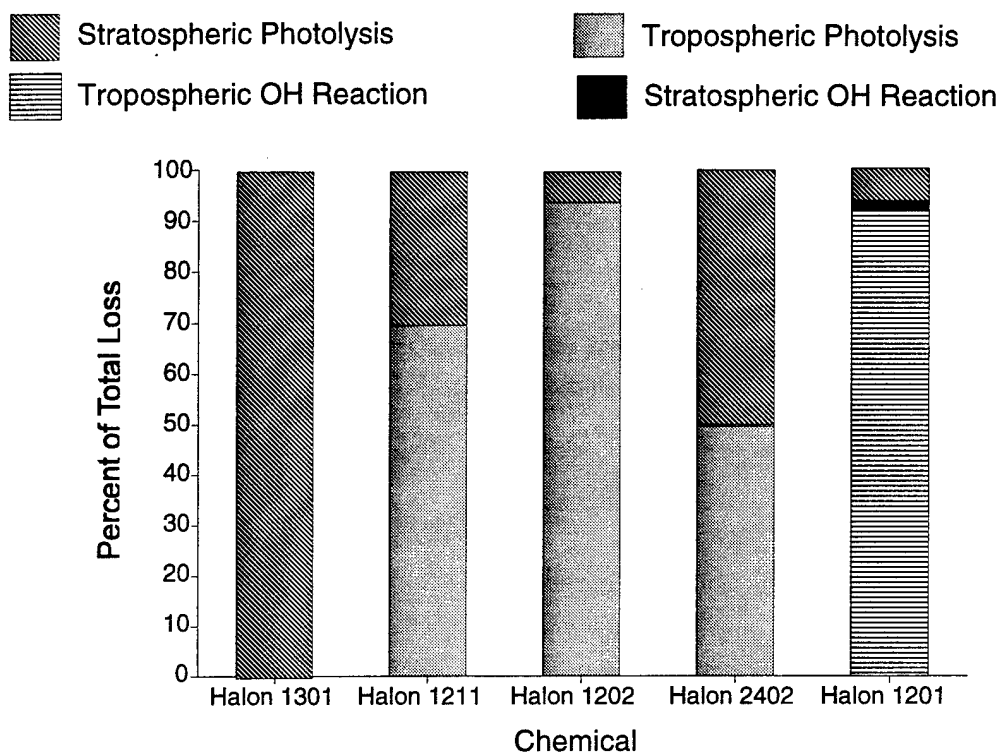
Figure 10. Atmospheric Removal Mechanisms for Halons.

TABLE 2. TROPOSPHERIC REMOVAL MECHANISMS.

Primary removal mechanism	Example families
Photodegradation	Iodides, carbonyls, bromides
Reaction with hydroxyl	Alkenes, aromatics, hydrogen-containing amines, hydrogen-containing ethers, carbonyls
Physical removal	Ketones, alcohols, esters
Reaction with tropospheric ozone	Alkenes
Thermal decomposition	[a]Reactive molecules (e.g., epoxides, peroxides)
Hydrolysis	[a]Compounds with direct silicon to halogen bonds, carbonyl halides

[a]Of little or no interest as halon replacement candidates.

SECTION IV

TOXICITY OF HALOCARBONS

The following is an overview of halocarbon and fire suppressant toxicity issues as abstracted from a report written by one of the authors of the present report (Reference 1).[*] Much of the detailed toxicology and safety information presented in this report was taken from Sax and Lewis (Reference 32) and from the National Institute for Occupational Safety and Health (NIOSH) *Registry of Toxic Effects of Chemical Substances* (Reference 33). The SAX Hazard Rating (HR) has been given for some compounds. This rating indicates the relative hazard for toxicity, fire, and reactivity with 3 denoting the worst hazard level. It should be noted, however, that careful consideration of the actual threat may indicate that a lower rating may be more appropriate for some compounds. For example, in some cases only toxicity by intraperitoneal, subcutaneous, and/or intravenous routes (only indirectly related to toxicities of interest here) are known. Moreover, emission of toxic combustion products appears to have been given undue weight. As an example, bis(trifluoromethyl)benzene is given a SAX Hazard Rating of 3, apparently based only on the fact that when heated with nitric and sulfuric acids, it emits explosive vapors, and when heated to decomposition, it emits "toxic fumes of F-" (apparently referring to HF formation [Reference 32]).

A.   ACUTE TOXICOLOGICAL INDICES

Table 3 contains a summary of acute toxicological indices, which are discussed in more detail in the following text.

---

[*]Stephanie R. Skaggs, now at Pacific Scientific HTL, also contributed much of the material used in this section.

TABLE 3. ACUTE TOXICOLOGICAL INDICES.

	Exposure limit	Definition
ALC	Approximate Lethal Concentration	The approximate concentration considered to cause death, similar to LC_{LO} but often used in place of LC_{50} when making assessments.
LC_{50}	Lethal Concentration-50%	Concentration causing death in 50% of an animal test population.
LC_{LO}	Lethal Concentration-Low	The lowest observed lethal concentration.
LD_{50}	Lethal Dose-50%	Dose causing death in 50% of an animal test population.
LD_{LO}	Lethal Dose-Low	The lowest observed lethal dose.
AD_{50}	Anesthetic Dose-50%	Concentration causing anesthesia in 50% of an animal test population.
LOAEL	Lowest Observed Adverse Effect Level	The lowest exposure level that has been observed to cause an adverse effect. For inhalation of halocarbons, the effect is usually cardiac sensitization.
NOAEL	No Observed Adverse Effect Level	The highest exposure level that has been observed to cause no adverse effect. For inhalation of halocarbons, the effect is usually cardiac sensitization.

1.   Lethality

The LC_{50} is defined as the concentration required to cause death in 50 percent of an animal test population. The Approximate Lethal Concentration (ALC) value was first established by DuPont, but is now used by other chemical manufacturers. The ALC approximates the lowest concentration that causes death (LC_{LO}). Thus, it is lower than the LC_{50} value. The ALC value is often used in place of the LC_{50} in assessing safety.

2.   Anesthesia

Anesthesia is the condition of loss of consciousness, usually coupled with the loss of response to pain and other stimuli. General anesthesia results from a depression of the central

nervous system (CNS), which can be exerted by a wide range of chemicals. Anesthetic potency of chemicals is tested in animals by observing decreases in righting reflex (ability to stand up after being knocked over) or diminished response to foot or tail shock. The AD_{50} is the calculated value corresponding to the concentration at which 50 percent of the test animals experience anesthesia. In AD_{50} experiments, anesthesia is defined as loss of the righting reflex or lack of response to shock. Anesthetic potency or mild CNS depression can also be observed in humans using performance decrement studies. Structure-activity relationships have been developed for predicting anesthetic effects (Reference 34).

3.   Cardiac Sensitization

Cardiac sensitization is the term used for the sudden onset of cardiac arrhythmias caused by a sensitization of the heart to epinephrine (adrenaline) in the presence of some concentration of a chemical. When comparing concentrations necessary to elicit acute toxic responses such as anesthesia, cardiac sensitization, or lethality, cardiac sensitization usually occurs at a lower concentration for halocarbons than other acute toxicity endpoints. Therefore, regulatory and standard-making authorities have used inhalation cardiac sensitization thresholds as the criterion for determining acceptability for use in areas where human occupancy may occur. The phenomenon of cardiac sensitization is particularly important in firefighting because under the stress of the fire event, higher levels of epinephrine are secreted by the body, increasing the possibility of sensitization.

The threshold level is the lowest concentration at which cardiac sensitization occurs. No definitive rule exists indicating the number of animals that must experience a marked response to determine the threshold value. In most cases, even one animal experiencing a marked response constitutes establishment of a threshold value. This level is also called the Lowest Observed Adverse Effect Level (LOAEL). The highest concentration at which no marked responses occur is called the No Observed Adverse Effect Level (NOAEL). While it is not known with certainty whether the LOAEL and NOAEL in dogs accurately represent these values in humans, the dog is the preferred animal model for determining cardiac physiology.

28

It should be noted that the cardiac sensitization LOAEL and NOAEL concentrations are conservative. They entail measurement of cardiotoxic effects in animals made sensitive to these effects by the administration of epinephrine. The administered epinephrine doses are just below the concentration at which epinephrine alone would cause cardiotoxicity in the experimental animal and are approximately ten times greater than the concentration a human would be likely to secrete under stress. Thus, LOAEL and NOAEL values are conservative even in high-stress situations.

B.   SUBCHRONIC AND CHRONIC TESTS

1.   90-Day Subchronic Toxicity Test

The 90-day subchronic toxicity test is an assay that determines pathological changes due to repeated and prolonged chemical exposure. Subchronic toxicity testing provides the basis for developing industrial exposure standards.

2.   Chronic Toxicity Testing

Chronic toxicity tests are conducted over the greater part of the animals lifespan (1.5 to 2 years in mice and 2 or more years in rats), starting at weaning. Daily exposure to the test agent occurs. The principal endpoint is tumor formation, as determined by histological exam.

3.   Carcinogenicity Screening

Chemical carcinogenesis is usually the result of long-term exposure to a chemical that may occur generally during industrial processing and handling. To determine the potential carcinogenicity of an agent, genotoxicity (mutagenicity) screening tests are often performed. Positive mutagenicity results alert toxicologists to the possibility of carcinogenesis and indicate the need for subchronic exposure testing to develop industrial exposure standards. While there are many tests used, the following genotoxicity tests are most commonly used.

a)   Ames Test

The Ames test, an *in vitro* test for mutagenicity, and by implication, carcinogenicity, uses mutant strains of bacterium *Salmonella typhimurium* as a preliminary screen for carcinogenic potential (Reference 35). A number of assays comprise the Ames test, and positives indicate that a mutation in the genetic material has occurred. Mutagenic and presumed carcinogenic materials cause genetic mutations that allow the bacterial strains to grow in a histidine-free medium.

b)   Mouse Lymphoma Test

The mouse lymphoma test, also an *in vitro* screening test, uses cell cultures of mouse lymphoma cells. The mutagenic potential of a material is tested by observing the ability to confer resistance within this cell line to normally toxic agents. Mutations in the genetic material allow the cells to grow in the presence of other known toxic materials (purines, pyrimidines, or ouabain). Promutagens (mutagenic agents that require metabolic activation) can also be identified.

c)   Mouse Micronucleus Test

The mouse micronucleus test, an *in vivo* test, determines the potential of a chemical to cause chromosome breakage or interference with normal cell division. The test entails exposing live mice to the test material, then removing premature red blood cells from the bone marrow, and observing the cells for the presence of chromosome fragments or the lack of signs of normal cell division. This test is not considered the most sensitive test for chromosomal aberrations.

C.   EXPOSURE LIMITS

Four major noncommercial organizations establish or recommend occupational exposure limits. The National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) are governmental organizations. Standards

30

established under OSHA are enforceable; however, NIOSH only sets recommended occupational exposure limits. Non-governmental organizations establishing exposure limits are the American Conference of Governmental Industrial Hygienists (ACGIH) and the American Industrial Hygiene Association (AIHA). Table 4 gives the various exposure limits that have been established. Note that most of these levels are not used extensively and are not well developed. The only ones with significant use by industrial hygienists are the PEL, the WEEL, and the TLV, which are the appropriate upper exposure limit for safe handling over a lifetime of occupational exposure (e.g., industrial processing, rather than fire fighting). The Acceptable Exposure Limit (AEL), which is widely cited, was originally used by DuPont; however, it is now given by a number of other commercial organizations.

Of greater importance in fire protection are the limits established for exposure during agent discharge. Two somewhat different sets of criteria have been established for total-flood protection.

The original 1994 National Fire Protection Association (NFPA) 2001 Standard on "Clean Agent Fire Extinguishing Systems" required that the design concentration for total flooding of a normally occupied area by halocarbons not exceed the cardiac sensitization NOAEL level (Reference 36). In addition, halocarbon agent concentrations above 24 percent were not allowed in normally occupied areas. The 1996 NFPA Standard 2001 (Reference 37) now allows the use of a halocarbon agent up to the LOAEL value for Class B hazards in normally occupied areas where a predischarge alarm and time delay are provided. The time delay must be set to ensure that occupants have time to evacuate prior to the time of discharge. The 2001 Standard calls for avoidance of unnecessary exposure to agents covered and for suitable safeguards to ensure prompt evacuation; however, no specific evacuation time is required. Audible and visual pre-discharge alarms are required.

The U.S. Environmental Protection Agency (EPA) Significant New Alternatives Policy (SNAP) program uses the cardiotoxic LOAEL value to assess total-flood use of an agent in normally occupied areas (Reference 38). Furthermore, the EPA uses OSHA Standard 1910.162 (Reference 39) for Halon 1301 as a basis for EPA's fire suppression use conditions. The EPA

TABLE 4. EXPOSURE LIMIT DEFINITIONS.

Exposure limit		Establishing organization	Definition
Long-Term Exposures			
AEL	Acceptable Exposure Limit	Commercial	
PEL	Permissible Exposure Limit	OSHA	Enforceable 8-hr Time-Weighted Average (TWA) exposure limit for airborne substances intended to reduce a significant risk of health or functional capacity impairment
REL	Recommended Exposure Limit	NIOSH	Similar to TLV values
TLV	Threshold Limit Value	ACGIH	TWA exposure limits similar to PEL values.
WEEL	Workplace Environmental Exposure Limit Guide	AIHA	Similar to TLV values.
WGL	Workplace Guidance Level	EPA	8-hr day TWA value analogous to PEL values.
Short-Term Exposures			
CL	Ceiling Level	OSHA	Enforceable exposure level that cannot be exceeded for any time period.
STEL	Short-Term Exposure Limit	OSHA	Enforceable 15-min TWA exposure that should not be exceeded at any time during a work day.
IDLH	Immediately Dangerous to Life and Health	NIOSH	Maximum concentrations from which one could escape within 30 min without experiencing escape-impairing or irreversible health effects.
EGL	Emergency Guidance Level	EPA	Applies to a short-term exposure of 15 or 30 min and is similar to the IDLH.

has applied the following:[*] (1) where egress from an area cannot be accomplished within one minute, the employer shall not use this agent in a concentration exceeding its NOAEL; (2) where egress takes longer than 30 seconds but less than one minute, the employer shall not use the agent in a concentration greater than its LOAEL; and (3) Agent concentrations greater than the LOAEL are only permitted in areas not normally occupied by employees provided that any employee in the area can escape within 30 seconds. Thus, unlike the NFPA, the EPA requires rigorous time limits for evacuation from areas where a total-flood discharge is used.

---

[*]Personal communication, K. Metchis, U.S. EPA, to C. Grant, NFPA, 20 September 1994.

SECTION V

IODIDES

A large amount of work has already been performed on the assessment and testing as iodides as Halon 1211 replacements, and an overview has been presented (Reference 40). Although iodides are tropodegradable compounds, they are not being considered as candidates in this report. Only a very brief review is given here.

On May 13, 1993, a group of interested users met during the 1993 Halon Alternatives Technical Working Meeting in Albuquerque, New Mexico, to decide whether and how to pursue the positive lead represented by one of the fluorinated iodides, trifluoromethyl iodide (CF_3I). Initial members of the group were the USAF, U.S. Army, U.S. Navy, the North Slope Oil and Gas Producers, and Pacific Scientific Company. This group developed a series of five tasks aimed at identifying potential "show stoppers," which would prevent the ultimate development of CF_3I as a halon replacement.

Follow-up meetings occurred throughout 1993 and 1994 to present the work of the New Mexico Engineering Research Institute (NMERI), National Institute of Standards and Technology (NIST), USAF, U.S. Army, U.S. Navy, Naval Research Laboratory (NRL), and others who were evaluating CF_3I. The results were presented at conferences held by the Working Group (References 41 and 42).

The testing efforts confirmed the laboratory-scale fire suppression and explosion inertion data, determined key acute toxicological information, assessed global environmental characteristics, identified manufacturing sources for developmental quantities of agent, and determined agent stability and materials compatibility properties (Reference 43). The n-heptane cup-burner concentration was 3.1 percent and the propane inertion concentration at peak flammability was 6.2 percent. The atmospheric lifetime is less than 1 day, the ODP is less than 0.008 and more likely 0.0001, and the 20-year GWP is less than 5 relative to CO_2 (Reference 44). Toxicological tests showed that CF_3I has a low order of acute toxicity with the 15-minute rat LC_{50} equal to 27.4 percent. The dog cardiac sensitization NOAEL was 0.2 percent; the LOAEL

was 0.4 percent. Since the expected design concentration will be in the range of 5 to 7 percent, the cardiotoxicity profile precludes the use of CF_3I for total-flood applications in normally occupied areas. However, CF_3I is still a highly promising replacement for unoccupied areas and in selected streaming applications.

Based on these findings, CF_3I moved from a laboratory material to being commercially available in bulk. Medium and large-scale testing in a number of applications have been carried out. Blends with other halocarbons have also been evaluated as streaming agents (References 45 and 46). The chemical is now being commercialized.

Unfortunately, work indicates that higher molecular weight fluoroiodocarbons were unlikely to have the potential of CF_3I due to toxicity concerns (Reference 40). Initial "range finder" or limit tests using rats have shown the ALC for perfluoropropyl iodide ($CF_3CF_2CF_2I$) is somewhere in the range of 3 to 5 percent. The 15-min LC_{50} is 4.9 to 6.2 percent (Reference 47), and the 2-hour mouse LC_{50} is 3.3 percent (Reference 33). The cardiac sensitization values are less than 0.1 percent for the NOAEL and 0.1 percent for the LOAEL.*

One area that may need further investigation is nonfluorinated alkyliodides. Note, however, that alkyliodides are strong alkylating agents and are often mutagenic or carcinogenic. Methyl iodide (CH_3I) is reported as moderately toxic by inhalation (rat LC_{50} = 1300 mg/m^3 [0.02 percent] for a 4-hour exposure) and skin contact and is a suspected carcinogen (Reference 32). It is also an experimental neoplastigen and tumorigen and a human skin irritant. Ethyl iodide (CH_3CH_2I) is reported to be mildly toxic by inhalation (rat LC_{50} = 65,000 mg/m^3 [1 percent] for a 30-min exposure). n-Propyl iodide has a 30-min rat LC_{50} = 70,000 mg/m^3 (1.0 percent) for a 30-min exposure. Isopropyl iodide (CH_3CHICH_3) has a relatively low toxicity by inhalation (rat LC_{50} = 320,000 mg/m^3 [4.6 percent] for a 30-min exposure). Note that the inhalation toxicity decreases as the alkyl group chain increases in length. Of some interest is the relatively large difference in the LC_{50} values for the n-propyl and isopropyl derivatives.

---

*"Toxicological Test Results," Huntington Research Center, UK, 1994 (unpublished results).

SECTION VI
BROMOALKANES

A.   CHEMISTRY

Bromoalkanes have been considered for some time as possible halon replacements within this project; however, they had been downgraded as prospects due to concerns about flammability and toxicity. Recent reviews, however, indicate that some saturated bromoalkanes appear to have lower than expected toxicities. For example, the 30-min rat LC_{50} for 1-bromopropane (n-propylbromide, $CH_3CH_2CH_2Br$) is 5.03 percent (Reference 32), and this value seems to increase as the alkyl group becomes larger.

In some preliminary testing, it was found that 1-bromopropane could not be ignited with a match even though the material is listed as flammable. In view of this, several extinguishment tests were run using the NMERI Laboratory-Scale Discharge Extinguishment (LSDE) apparatus, which showed that the 1-bromopropane effectively extinguished a 4- by 4-inch pan fire using n-heptane fuel (Reference 48).

Although the production of hydrobromofluorocarbons (HBFC) and bromofluorocarbons (BFC, e.g., Halon 1301) has been banned under the Montreal Protocol, there is still a possibility that bromoalkanes in general may not be regulated. It must be noted, however, that methyl bromide, which has agricultural and fumigation applications, is regulated under the Montreal Protocol. On the other hand, due to the greater number of hydrogen atoms, it is expected that higher molecular weight materials will have a lower atmospheric lifetime and ODP than methyl bromide ($t_{1/e}$ = 1.3 years, ODP = 0.64; Reference 10). Although bromoalkanes are still somewhat unlikely to prove acceptable, it is prudent to perform a review of the toxicity of these compounds.

B. TOXICITY

Table 5 contains an overview of toxicological and safety information (with an emphasis on inhalation toxicity and flammability) for bromoalkanes (References 32 and 33). This review is not comprehensive, and only the most important information is cited. Because of the variation in species and time, it is difficult to judge the trends in inhalation toxicity as the molecular weight increases. Certainly, bromomethane is much more toxic than the other compounds. It appears that for short-term exposures, the LC_{50} values for compounds other than bromomethane are 4 to 15 percent. The relatively low LC_{50} of 0.7 percent reported for 2-bromopropane cannot be assessed since neither the mammalian species nor the time period is given.

TABLE 5. TOXICOLOGICAL AND SAFETY INFORMATION FOR BROMOALKANES.

Compound	Formula	CAS No.	Observations[a]
Bromomethane	CH_3Br	74-83-9	[BNM500] LC_{LO} (man, inhalation, 2 hr) = 60,000 ppm, LC_{50} (rat, inhalation, 8 hr) = 302 ppm. Human poison by inhalation. Experimental carcinogen by ingestion. Human systemic effects by inhalation: anorexia, nausea, vomiting. Corrosive to skin, can produce severe burns. Hemotoxic and narcotic with delayed action. Effects are cumulative and damaging to nervous systems. Reported to be eight times more toxic on inhalation than ethyl bromide. HR = 3
Bromoethane	CH_3CH_2Br	33473	{RTECS KH6475000} LC_{LO} (rat, inhalation, 15 min) = 148,000 ppm (14.8%), LC_{50} (mouse, inhalation, 1 hr) = 16,230 ppm. [BNI250] Moderately toxic by ingestion. Mildly toxic by inhalation. Eye, skin irritant. Anesthetic, narcotic. Vapors markedly irritating to the lungs even for short periods. Dangerously flammable and moderately explosive. HR = 3.

TABLE 5. TOXICOLOGICAL AND SAFETY INFORMNATION FOR BROMOALKANES (concluded).

Compound	Formula	CAS No.	Observations[a]
1-Bromopropane	$CH_3CH_2CH_2Br$	106-94-5	{RTECS TX4110000} LC_{50} (rat, inhalation, 30 min) = 253,000 mg/m^3 (5.03%). [BNX750] Moderately toxic by ingestion. Mildly toxic by inhalation. Dangerous fire hazard. HR = 2.
2-Bromopropane	$CH_3CHBrCH_3$	75-26-3	{RTECS TX4111000} LC_{50} (mammal, inhalation) = 36 g/m^3 (0.7%). [BNY000] Flash point < 14 °C. Dangerous fire hazard.
1-Bromobutane	$CH_3CH_2CH_2CH_2Br$	109-65-9	{RTECS EJ6225000} LC_{50} (rat, inhalation, 30 min) = 237,000 mg/m^3 (4.23%). [BMX500] Dangerous fire hazard. HR = 3.
1-Bromo-2-methylpropane	$CH_2BrCH(CH_3)CH_3$	78-77-3	[BNR750] LC_{LO} (mammal, inhalation) = 50,500 mg/m^3 (0.90%). Moderately toxic by intraperitoneal. Mildly toxic by inhalation. Experimental neoplastigen. Dangerous fire hazard. Flash point = 22 °C. HR = 3.
2-Bromo-2-methylpropane	$CH_3CBr(CH_3)CH_3$		[BNS000] No toxicity data. Dangerous fire hazard. Flash point = -18 °C.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference; the RTECS Number (Reference 33) is given in braces, again followed by information from that source. "HR" denotes the SAX Hazard Rating.

SECTION VII

ALKENES

A. CHEMISTRY

The alkenes contain C-C double bonds, which consist of a σ bond plus a $p\pi \leftrightarrow p\pi$ bond (Figure 11).
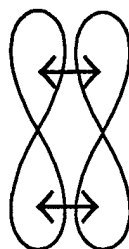
Figure 11. $p\pi \leftrightarrow p\pi$ Bonding.

1. Properties

A report by the National Institute of Standards and Technology (NIST) (Reference 49) lists several alkenes for fire suppression investigation. These compounds are shown in Table 6 with some name changes to make the compounds more recognizable to chemists. The physical properties are given in Table 7. It should be noted that this report did not select halon replacement candidates, but rather prepared an "Exploratory List" covering a variety of chemical families to use in a study of fire suppression mechanisms and measurement techniques. Few of the compounds listed in the complete NIST report could be considered as candidates due to toxicity and other concerns.

TABLE 6. NIST EXPLORATORY LIST OF ALKENES.

Name	Formula	CAS No.
[a]Hexafluoropropene	$CF_2=CFCF_3$	116-15-4
[a,b]Octafluoro-2-butene	$CF_3CF=CFCF_3$	360-89-4
[a]1,1,3,3,3-Pentafluoro-1-propene	$CF_3CH=CF_2$	690-27-7
[a]1,1,1-Trifluoro-3-propene	$CF_3CH=CH_2$	677-21-4
[a,b]1,2-Bis(nonafluoro-n-butyl)ethene	$(n\text{-}C_4F_9)CH=CH(n\text{-}CH_4F_9)$	84551-43-9
3-Bromo-1,1,2,3,3-pentafluoro-1-propene	$CF_2BrCF=CF_2$	431-56-1
[b]1-Bromo-1,2,3,3,3-pentafluoro-1-propene	$CF_3CF=CFBr$	14003-53-3
[b]1,1,1,4,4,4-Hexafluoro-2-butene	$CF_3CH=CHCF_3$	66711-86-2
[b]1-Bromo-1,1,4,4,4-pentafluoro-2-butene	$CF_2BrCH=CHCF_3$	Not available
[b]2-Bromo-1,1,1,4,4,4-hexafluoro-2-butene	$CF_3BrC=CHCF_3$	400-41-9
1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)butene	$(CF_3)_2C=C(CF_3)_2$	360-57-6

[a]Commercially available.
[b]Isomer not identified.

2.   Synthetic Routes

Trifluoromethyl groups (-CF$_3$) can be attached to alkyl bromides, including alkenes, by reaction with CF$_3$I in the presence of copper (Reference 50). The reaction is similar to that reported for attachment of fluoroalkyl groups to aromatic rings (Reference 51). An example is shown in Reaction 10 for addition of -CF$_3$ to 1-bromo-2-phenylethene.

$$(C_6H_5)CH=CHBr + CF_3I \xrightarrow{\text{copper}} (C_6H_5)CH=CHCF_3 \qquad (10)$$
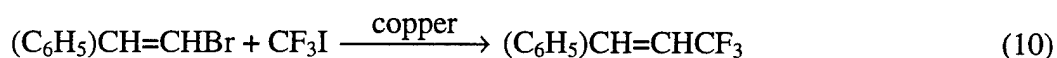
The Wittig reaction (Reaction 11) provides general purpose synthesis of alkenes from appropriately substituted carbonyl compounds.

$$R'_3P=CH_2 + R_2C=O \rightarrow R'_3P=O + H_2C=CR_2 \qquad (11)$$

TABLE 7. PROPERTIES OF ALKENES IN NIST EXPLORATORY LIST.

Formula	Boiling point, °C	Vapor pressure, atm at 298 K	Heat capacity, J/mol-K at 298 K	Heat of vaporization, kJ/mol at boiling point
$CF_2=CFCF_3$	-29	6.42	116	21
$CF_3CF=CFCF_3$	0	2.62	[a]138	[a]21
$CF_3CH=CF_2$	-21	[a]5	[a]109	[a]23
$CF_3CH=CH_2$	-17	[a]4	[a]92	[a]24
$(n\text{-}C_4F_9)CH=CH(n\text{-}CH_4F_9)$	132	[a]0.006	[a]377	[a]36
$CF_2BrCF=CF_2$	28	[a]1	[a]121	[a]27
$CF_3CF=CFBr$	[a]30	[a]1	[a]121	[a]27
$CF_3CH=CHCF_3$	6	[a]1.6	[a]130	[a]26
$CF_2BrCH=CHCF_3$	[a]57	[a]0.1	[a]138	[a]30
$CF_3BrC=CHCF_3$	[a]65	[a]0.06	[a]143	[a]33
$(CF_3)_2C=C(CF_3)_2$	55	[a]0.28	180	29

[a]Estimated (Reference 49).

The interesting unsaturated compound $F_2C=NH$, of some possible interest, has been prepared by controlled hydrolysis of trifluoromethyl isocyanate (CF_3NCO) in triethylamine ($N(C_2H_5)_3$) (Reference 52). The ^{13}C, ^{19}F, and ^1H nuclear magnetic resonance (NMR) spectra are reported, and the IR gas and IR matrix spectra are discussed in terms of a normal coordinate analysis. The photoelectron spectrum of $F_2C=NH$ is compared with those of $F_2C=NF$ and $H_2C=NH$ revealing a strong fluoro effect. In the solid state, $F_2C=NH$ is aggregated to infinite zigzag chains by N-H hydrogen bonding.

3.   Flammability

Lower flammability limits (LFL) of several haloalkenes considered as anesthetics have been reported (Reference 34; Table 8). It is interesting to note that the flammabilities in pure oxygen are not too dissimilar from those in air.

TABLE 8. LOWER FLAMMABILITY LIMITS OF SOME HALOALKENES.

Compound	LFL, % by volume	
	Air	Oxygen
$CH_3CH=CClCH_3$	2.3	a
$CF_2CH_2OCH=CH_2$	4.4	4.0-4.5
$CH_3CCl=CH_2$	4.5	4.5
$CF_2=CHF$	17.4	a
$CHCl=CHCl$	9.7	10
$CHCl=CCl_2$	10.5	7.5
$CF_3CCl=CH_2$	a	5
$CF_3CBr=CH_2$	b	7
$CF_2=CFCl$	b	8.4

[a]Not available.
[b]Not flammable in air.

B. ENVIRONMENTAL CHARACTERISTICS

For the haloalkenes that have been studied, reactions with •OH proceed by addition to the double bond (Reaction 5), with the hydrogen atom abstraction being essentially negligible. When chlorine or bromine is attached to the double bond, it can be lost from the final product to give an alkenyl alcohol (Reaction 12, where X is a bromine or a chlorine atom). This reaction is endothermic, and therefore unlikely, for fluorine atoms attached at the double bond (Reference 19).

$$X-\overset{\underset{\displaystyle |}{OH}}{\underset{\displaystyle |}{C}}-C\overset{*}{\diagup}\diagdown \longrightarrow \quad \overset{HO}{\diagdown}C=C\overset{\diagup}{\diagdown} + \ •X \qquad (12)$$

42
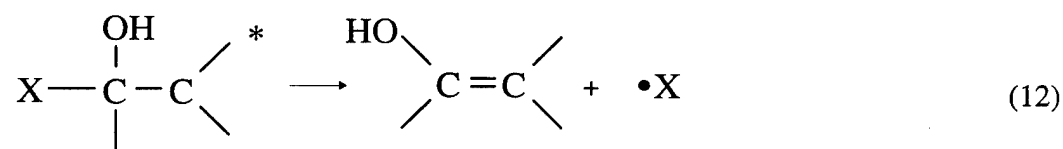
The reaction rates of haloalkenes with hydroxyl radicals range from approximately 10^{-13} to 10^{-11} cm^3/molecule-s compared with approximately 10^{-15} to 10^{-12} cm^3/molecule-s for saturated halocarbons (Reference 19).* On an average, the reactions are about 100 times faster for alkenes than for alkanes, and the atmospheric lifetimes are reduced accordingly. Thus, from atmospheric lifetimes on the order of 10 years for a typical HCFC (Table 1), one would predict atmospheric lifetimes of approximately 1/10 year (about 1 month) for a typical haloalkene.

One can also estimate reaction rate constants and atmospheric lifetimes using the method of Wuebbles and Connell (Reference 15). This has been done for a variety of bromoalkenes (Table 9). Several things should be noted. First, the addition of fluorine atoms at the double bond increases the atmospheric lifetime. Second, lifetime decreases when alkyl groups are placed at the double bond. Finally, photodecomposition due to the presence of bromine and, to a lesser extent, the reaction of compounds containing hydrogen with tropospheric hydroxyl free radicals will lower the lifetimes. These approximations indicate that lifetimes for compounds of interest will range from 3 months down to less than a day.

A more precise calculation is possible from experimental rate constants and Equation 7; however, the only fluoroalkene whose reaction rate constant with hydroxyl free radicals has been determined is CH$_2$=CHF, where k_{OH} is 5.56 x 10^{-12} cm^3/molecule-s at 299 K (Reference 19). Using this value and a globally averaged hydroxyl free radical concentration of 9.7 x 10^5 molecules/cm^3 (Reference 14), one calculates a lifetime of approximately 2 days (1/(5.56 x 10^{-12})(9.7 x 10^5) seconds).

Removal by reaction with tropospheric ozone is also possible for alkenes. A number of halogenated alkenes have atmospheric lifetimes that range from less than 1 day to about 7 days as a result of the reaction with tropospheric ozone (Reference 53). The reaction is faster when alkyl groups (but not totally fluorinated alkyl groups) are substituted at the double bond. In the

---

*These rate constants are for 298 K (0 °C). This is a little higher than the actual average for tropospheric temperature; however, it is difficult to find reported or estimated rate constants at 265 K, the temperature that is closer to the average. Unless reported otherwise, assume that all rate constants in this report are for 298 K or approximately this temperature.

TABLE 9. ESTIMATED FIRST-ORDER RATE CONSTANTS FOR HYDROGEN ATOM ABSTRACTION AND ATMOSPHERIC LIFETIMES FOR SOME BROMOALKENES.

Compound	k_{OH}^2 [•OH], s^{-1}	Lifetime, days
$CF_2=CFBr$	1.3×10^{-7}	90
$CF_2=CFCF_2Br$	5.8×10^{-7}	19
cis-$CF_3CF=CFCF_2Br$	2.2×10^{-6}	5.4
trans-$CF_3CF=CFCF_2Br$	2.5×10^{-6}	4.6
$(CF_3)_2C=CFCF_2Br$	4.8×10^{-6}	2.4
$(CF_3)_2C=C(CF_3)CF_2Br$	1.5×10^{-5}	0.8
$CH_2=CFBr$	3.6×10^{-7}	32
$(CF_3)_2C=CHCF_2Br$	8×10^{-6}	1.4

Wuebbles and Connell approximation method (Reference 15), compounds with no alkyl substitution ($Y_2C=CY_2$) are given a base rate constant of 1.9×10^{-19} cm^3/molecule-s, compounds with one alkyl substituent at the double bond ($RYC=CY_2$) are assigned a base rate of 1.3×10^{-17} cm^3/molecule-s, and compounds with two alkyl substituents at the double bond ($RYC=CRY$) are assigned a base rate of 2.0×10^{-16} cm^3/molecule-s. Here, Y represents H, Cl or F and R is any non-totally-fluorinated alkyl group (Reference 15). These base rates are corrected when Y = Cl or F. In the Wuebbles and Connell method, a single chlorine atom at the double bond decreases the rate constant by a factor of 0.15, two geminal chlorine atoms reduce the constant by a factor of 0.002, and a single fluorine reduces the rate constant by a factor of 0.4. If one considers a compound from Table 9, e.g., $CF_2=CFCF_2Br$, a rate constant and an atmospheric lifetime using the globally averaged tropospheric ozone concentration of $[O_3] = 5.0 \times 10^{11}$ molecules/cm^3 can be calculated (Reference 15). For this compound, one calculates a first-order reaction rate constant of k = $(k_{O3})[O_3]$ = $(1.3 \times 10^{-17})(0.4)^3(5.0 \times 10^{11})$ = 4×10^{-7}. This allows a calculation for the atmospheric lifetime of $t_{1/e}$ = 1/k = 2.5×10^6 seconds or approximately 1 month. On the other hand, data presented elsewhere indicate that halogen substitution actually decreases the atmospheric lifetime in many cases (Reference 53). Whichever is correct, it is obvious that halogenated alkenes will react rapidly with tropospheric ozone. It must be realized, however,

44

that the fate of highly fluorine-substituted alkenes due to reaction with tropospheric ozone is still somewhat uncertain. Moreover, the Wuebbles and Connell estimation method is probably reliable only within a factor of 10 for reactions of alkenes with tropospheric ozone (Reference 15).

Taking all of this into account, haloalkenes (more importantly, fluoroalkenes) are expected to have tropospheric lifetimes on the order of days due to reaction with hydroxyl free radicals and ozone, and this is likely to be even lower with bromine substitution (Reference 54).

C. TOXICITY

As a result of their wide use in industry (Table 10), significant toxicological information is available on the haloalkenes. Unfortunately, however, most of these are chlorine-containing compounds, and less is known about the toxicity of the fluoroalkenes and bromofluoroalkenes, which are of greater interest here. It has been reported that bromine- and chlorine-substituted ethenes, propenes, and butenes show decreased irritation, decreased tissue damage, and decreased toxicity, but increased anesthetic potency when compared to the saturated analogs (Reference 55). Fluorinated alkenes having the general formula RCX=CXY, CXY=CXY, and RCX=CXR (where R is a fluoroalkyl group and X and Y are halogens) are reported to be toxic (Reference 34). Chloroalkenes exhibit a wide range of acute and chronic toxic effects (Reference 56). A number of the chloroalkenes have relatively low acute toxicities; however, several are known or suspected carcinogens and/or can cause damage to the liver (hepatotoxicity), kidneys, and central nervous system. The chloropropenes are strong irritants to the eyes, skin, and respiratory system, which can cause pulmonary edema. Table 11 gives toxicity information on selected alkenes related to compounds of interest (specifically compounds containing bromine and/or fluorine, Reference 32). Any boiling points (BP) shown in this table are for 760 Torr pressure unless otherwise noted. In all cases, available inhalation data are given. Table 12 gives a brief overview of the toxicity of the alkenes investigated by NIST (Reference 49).

45

TABLE 10. HALOALKENES USED IN INDUSTRY.

Formula	Chemical name	Application
$H_2C=CHCl$	Monochloroethene (vinyl chloride)	Plastics
$H_2C=CCl_2$	1,1-Dichloroethene (vinylidene chloride)	Copolymers
(structure: Cl, Cl on one carbon; H, H on other) $C=C$	*cis*-1,2-Dichloroethene	Organic syntheses, solvent
(structure: Cl, H; H, Cl) $C=C$	*trans*-1,2-Dichloroethene	Organic syntheses, solvent
$Cl_2C=CCl_2$	Tetrachloroethene	Dry cleaning, degreasing
$H_2C=CHCH_2Cl$	3-Chloropropene (allyl chloride)	Manufacturing intermediate
$HClC=ClCH_3$	1,2-Dichloropropene	Soil fumigant, solvent
$H_2C=CClCH=CH_2$	2-Chloro-1,3-butadiene (chloroprene)	Synthetic rubber
$Cl_2C=CClCCl=CCl_2$	Hexachlorobutadiene	Solvent, heat transfer

TABLE 11. TOXICITIES OF SELECTED ALKENES.

Compound	Formula	CAS No.	Observations[a]
3-Bromopropene	$CH_2=CHCH_2Br$	106-95-6	[AFY000] LC_{50} (rat, inhalation, 30 min) = 10,000 mg/m^3. Poison by ingestion, intraperitoneal. Mildly toxic by inhalation. BP = 71.3 °C, LEL = 4.4%, UEL = 7.3%. HR = 3.
3-Fluoropropene	$CH_2=CHCH_2F$		[AGG500] Poison by inhalation, ingestion. Strong irritant. BP = -10 °C. HR = 3.
2-Bromo-2-propenal	$CH_2=CBrCHO$	14925-39-4	[BMT000] Mutagenic data.
4-Bromo-1-butene	$CH_2=CHCH_2CH_2Br$	5162-44-7	[BMX825] No toxicity data reported. A dangerous fire hazard (flash point < 1 °C). HR = 3.

TABLE 11. TOXICITIES OF SELECTED ALKENES (continued).

Compound	Formula	CAS No.	Observations[a]
2-Bromo-2-chloro-1,1-difluoroethene	$CBrCl=CF_2$	758-24-7	[BNA000] LC_{50} (mouse, inhalation, 30 min) = 250 ppm. Moderately toxic by inhalation.
1-Bromopropene	$CHBr=CHCH_3$	590-14-7	[BOA000] Mutagenic data only.
2-Bromopropene	$CH_2=CBrCH_3$	557-93-7	[BOA250] Mutagenic data only.
Bromotrifluoroethene	$CBrF=CF_2$	598-73-2	[BOJ000] No quantitative toxicity data given. Poison. Flammable gas or liquid. Ignites spontaneously in air. HR = 3.
1-Chloro-3-bromo-1-butene	$CHCl=CHCH_2Br$	64037-53-2	[CES250] LD_{50} (rat, oral) = 74 mg/kg, LD_{50} (mouse, oral) = 56,500 µg/kg. Poison by ingestion. HR = 3.
3-Chloro-2-fluoro-1-propene	$CH_2=CFCH_2Cl$	6186-91-0	[CHJ250] LC_{LO} (rat, inhalation, 4 hr) = 1000 ppm, LD_{50} (rat, oral) = 280 mg/kg, LD_{50} (rabbit, skin) = 200 mg/kg. Poison by ingestion, skin contact. Mildly toxic by inhalation. HR = 3.
Chlorotrifluoroethene	$CClF=CF_2$	79-38-9	[CLQ750] LC_{50} (rat, inhalation, 4 hr) = 1000 ppm, LC_{50} (mouse, inhalation, 7 hr) = 3000 ppm, LD_{50} (mouse, oral) = 268 mg/kg. Poison by ingestion, intraperitoneal. Moderately toxic by inhalation. Dangerous fire hazard. LEL = 24%, UEL = 40.3%, HR = 3.
1,4-Dibromo-2-butene	$CH_2BrCH=CH-CH_2Br$	6974-12-5	[DDL400] LC_{LO} (mouse, inhalation, 10 min) = 1260 mg/m^3, LD_{50} (rat, oral) = 75 mg/kg. Poison by ingestion, intraperitoneal. Moderately toxic by inhalation. Skin, severe eye irritant. HR = 3.

TABLE 11. TOXICITIES OF SELECTED ALKENES (continued).

Compound	Formula	CAS No.	Observations[a]
trans-1,4-Dibromo-2-butene	$CH_2BrCH=CH-CH_2Br$	6974-12-5	[DDL600] LD_{50} (rat, oral) = 62 mg/kg, LD_{50} (mouse, oral) = 29 mg/kg. Poison by ingestion. Severe skin irritant. HR = 3.
2,3-Dibromo-1-propene	$CH_2BrCBr=CH_2$	513-31-5	[DDL600] Poison by intravenous. HR = 3.
Dichlorodifluoroethene	[b]$C_2Cl_2F_2$	27156-03-2	[DFA200] Moderately toxic by inhalation. Skin, eye, mucous membrane irritant. HR = 2.
1,1-Dichloro-2,2-difluoroethene	$CCl_2=CF_2$	79-35-6	[DFA300] LC_{50} (rat, inhalation, 4 hr) = 505 mg/m^3, LC_{50} (mouse, inhalation, 4 hr) = 610 mg/m^3, LC_{50} (guinea pig, inhalation, 4 hr) = 700 mg/m^3. Moderately toxic by inhalation. HR = 2.
Heptafluoroisobutene methyl ether	$(CF_3)_2C=CFOCH_3$	360-53-2	[HAY500] LD_{50} (rat, oral) = 1070 mg/kg, LD_{50} (mouse, oral) = 1070 mg/kg. Poison by intraperitoneal, intravenous. Moderately toxic by ingestion. HR = 3.
Hexafluoropropene	$CF_2=CFCF_3$	116-15-4	[HDF000] LC_{50} (rat, inhalation, 4 hr) = 11,200 mg/m^3 (0.18%), LC_{50} (mouse, inhalation, 4 hr) = 750 ppm. Mildly toxic by inhalation. Nonflammable. Reported to react with tetrafluoroethene and air to form explosive peroxides. HR = 3.
1,1,1,2,3,4,4,4-Octafluoro-2-butene	$CF_3CF=CFCF_3$	360-89-4	[OBO000] LC_{LO} (rat, inhalation, 4 hr) = 6100 ppm. Nonflammable. Mildly toxic by inhalation. Mutagenic data. HR = 1.

48

TABLE 11. TOXICITIES OF SELECTED ALKENES (concluded).

Compound	Formula	CAS No.	Observations[a]
Octafluoroisobutene	$(CF_3)_2C=CF_2$	382-21-8	[OBM000] LC_{50} (rat, inhalation, 6 hr) = 500 ppb, LC_{LO} (mouse, inhalation, 2 hr) = 10 mg/m^3, LC_{50} (rabbit, inhalation, 2 hr) = 1200 ppb, LC_{50} (guinea pig, inhalation, 2 hr) = 1050 ppb. Deadly poison by inhalation. Skin, eye, mucous membrane irritant. HR = 3.
Tetrafluoroethene	$CF_2=CF_2$	116-14-3	[OBM000] LC_{50} (rat, inhalation, 4 hr) = 40,000 ppm, LC_{50} (mouse, inhalation, per kg) = 143 g/m^3. Mildly toxic by inhalation. Flammable. Explosive in absence of inhibitor. HR = 2
Bromoethene	$CH_2=CHBr$	593-60-2	[VMP000] LD_{50} (rat, oral) = 500 mg/kg. Moderately toxic by ingestion. Experimental carcinogen, neoplastigen, tumorigen. Dangerous fire hazard. HR = 3.
Fluoroethene	$CH_2=CHF$	75-02-5	[VPA000] poison. Gas ignites, may explode. LEL = 2.6%, UEL = 21.7%. HR = 3.
1,1-Difluoroethene	$CH_2=CF_2$	75-38-7	[VPP000] LC_{LO} (rat, inhalation, 4 hr) = 12,800 ppm. Mildly toxic by inhalation. Experimental neoplastigen. Very dangerous fire hazard. Vapor explosive when exposed to heat, flame. HR = 3.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.

[b]Isomer not designated.

TABLE 12. TOXICITY OF ALKENES IN NIST EXPLORATORY LIST.

Formula	[a]Hazard rating	[b]Toxicity comments
$CF_2=CFCF_3$	3	Mildly toxic by inhalation. 4-hour rat inhalation: $LC_{50} = 11200$ mg/m^3. 4-hour mouse inhalation: $LC_{50} = 750$ ppm. Mixtures of 50-75% produced mild anesthetic effects, but convulsions and delayed death occurred.
$CF_3CF=CFCF_3$	1	Mildly toxic by inhalation. 4-hour rat inhalation: $LC_{Lo} = 6100$ ppm. Note, however, that perfluoroisobutane is highly toxic by inhalation.
$CF_3CH=CF_2$	c	No toxicity data available.
$CF_3CH=CH_2$	c	No toxicity data available.
$(n$-$C_4F_9)CH=CH(n$-$CH_4F_9)$	c	Used as blood substitute; therefore, short term toxicity is expected to be satisfactory.
$CF_2BrCF=CF_2$	c	No toxicity data available.
$CF_3CF=CFBr$	c	No toxicity data available.
$CF_3CH=CHCF_3$	c	No toxicity data available. The perfluorobutyl analog is a blood substitute, and the toxicity of this compound may, therefore, be low.
$CF_2BrCH=CHCF_3$	c	No toxicity data available.
$CF_3BrC=CHCF_3$	c	No toxicity data available.
$(CF_3)_2C=C(CF_3)_2$	c	Tetrakis(perfluoro-n-butyl)ethene, a closely related compound, is a blood substitute, and the toxicity of this compound may, therefore, be low.

[a]Reference 32.
[b]Reference 49.
[c]Not available.

There may be significant differences in toxicities of isomers, e.g., 1,1-dichloroethene ($CCl_2=CH_2$) is reported to be a poison by inhalation with a SAX of 3 (Reference 32). On the other hand, the *cis* and *trans* isomers of 1,2-dichloroethene ($CHCl=CHCl$) are reported to be mildly toxic (HR = 1). Note, however, that in these two cases the exposure times and end points for the inhalation toxicity indices were significantly different, thus making comparisons difficult.

SECTION VIII

ALCOHOLS

A.   CHEMISTRY

Alcohols are oxygenated compounds in which a hydroxyl (-OH) group is attached to a hydrocarbon skeleton. Lower molecular weight alcohols (one or two carbons) include methanol (CH_3OH), ethanol (C_2H_5OH), and ethylene glycol ($C_2H_2(OH)_2$). Higher molecular weight alcohols include the propanols (C_3H_7OH), butanols (C_4H_9OH), and pentanols ($C_5H_{11}OH$). Various fluorinated compounds have been synthesized by replacing one or more of the hydrogen atoms with fluorine.

1.   Synthetic Routes

Reactions 13 and 14 have been used to produce fluorinated alcohols as candidates for replacement of ozone depleting substances (ODSs).[*] Reaction of (trifluoromethyl)trimethyl-silane ($Si(CH_3)_3(CF_3)$) with carbonyl compounds provides a general-purpose method for preparing compounds with -CF_3 groups on carbons alpha to -OH groups (Reference 57; Reaction 15).
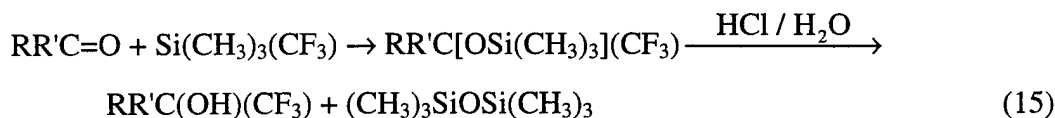
$$CH_3(CF_3)_2COH \xrightarrow{Cl_2} CCl_3(CF_3)_2COH \xrightarrow{SbF_5} CF_3(CF_2)_2COH \qquad (13)$$

$$CF_3CF_2I + CF_3CHO \xrightarrow{CF_3Li} CF_3CF_2CH(OH)CF_3 \qquad (14)$$

$$RR'C=O + Si(CH_3)_3(CF_3) \rightarrow RR'C[OSi(CH_3)_3](CF_3) \xrightarrow{HCl/H_2O}$$
$$RR'C(OH)(CF_3) + (CH_3)_3SiOSi(CH_3)_3 \qquad (15)$$

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

B. ENVIRONMENTAL CHARACTERISTICS

The two primary paths for removal of alcohols from the atmosphere are hydrogen atom abstraction by hydroxyl free radicals and rainout.

1. Hydrogen Atom Abstraction

For a compound such as CH_3OH, hydrogen atom abstraction by hydroxyl free radicals can occur from either the alkyl group (Reaction 16) or the hydroxyl group (Reaction 17). In general, abstraction by both pathways is observed, and the relative importance depends on the structure of the alcohol and the reaction temperature (Reference 19).

$$CH_3OH + \bullet OH \rightarrow \bullet CH_2OH + H_2O \qquad (16)$$

$$CH_3OH + \bullet OH \rightarrow CH_3O\bullet + H_2O \qquad (17)$$

The addition of an OH group to a carbon atom containing a hydrogen atom greatly increases the reaction rate for abstraction of that hydrogen atom by hydroxyl free radical. This can be seen in the reaction rate constants for methane, CH_4, of 1.8×10^{-14} cm^3/molecule-s and methyl alcohol, CH_3OH, 1×10^{-12} cm^3/molecule-s (Reference 19).

A limited amount of information on atmospheric lifetimes and GWPs of fluorinated alcohols is available (Table 13). Insufficient details have been reported, however, to judge the reliability of the values given.[*] The atmospheric parameters for $(CH_3)_3COH$ in Table 13 appear to be incorrect. The atmospheric lifetime seems to be far too long. The rate constant for reaction of this compound with hydroxyl free radicals is approximately 1/5 that for reaction of $(CH_2)_2CHOH$ (Reference 19), but the atmospheric lifetime is reported as 350 times higher for $(CH_3)_3COH$. The approximation method of Wuebbles and Connel (Reference 15), gives an

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

estimated lifetime for $(CH_3)_3COH$ of 131 days based on hydrogen abstraction alone. It may be that the paper cited[*] contains a misprint of "years" for "days."

TABLE 13. ATMOSPHERIC ENVIRONMENTAL PARAMETERS FOR FLUORINATED ALCOHOLS.

Compound	Lifetime, years	GWP based on CFC-11	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
[a]$(CH_2)_2CHOH$	0.32	0.005	79	24	8
[a,b]$(CH_3)_3COH$	113.13	2.29	5543	6144	3232
CF_3CH_2OH	0.16	0.006	86	26	8
$CF_3CF_2CH_2OH$	0.57	0.01	135	25	13
[c]$(CF_2)_4CH(OH)$	2.18	0.03	519	159	50
CF_3CH_2OH	0.55	0.01	123	38	12
$(CF_3)_2CHOH$	2.60	0.04	637	195	61
$CF_3CF_2CH_2OH$	0.60	0.01	145	44	14

[a]Non-fluorinated alcohol included for comparison.
[b]This value is highly suspect (see text).
[c]The formula indicates that this is a cyclopentanol, although the structure was not given.

An extensive amount of work has been performed on atmospheric decomposition of trifluoromethyl alcohol (CF_3OH) since it is of importance as a product from the photo-oxidation of many of the halocarbon ODS replacements. Unfortunately, however, the chemistry of CF_3OH is quite different from that of many other fluorinated alcohols, since this compound is inherently unstable, breaking down by a 1,2-elimination of hydrogen fluoride (HF) to give carbonyl fluoride (COF_2) (Reaction 18). Thus, it is difficult to reliably apply observations on the atmospheric fate of this compound to the fate of other fluorinated alcohols. Quantum mechanical *ab initio* calculations of activation energies and thermodynamic stabilities for the various

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

53

decomposition channels show that Reaction 18 is the kinetically and thermodynamically most favorable decomposition pathway (Reference 58). The fate of CF_3OH in the stratosphere has been reviewed (Reference 59). This alcohol will undergo hydrogen abstraction by •OH free radicals (Reaction 19); however, this does not appear to cause a significant loss in the stratosphere. Homogeneous thermal decomposition (Reaction 18) has a high calculated activation energy of 47.9 kcal/mol (Reference 60); however, heterogeneous decomposition on stratospheric aerosols may be effective. In the troposphere, CF_3OH is expected to be incorporated into water droplets, where hydrolysis will occur to give HF and CO_2 (Reference 61).

$$CF_3OH \rightarrow HF + COF_2 \tag{18}$$

$$CF_3OH + •OH \rightarrow CF_3O• + H_2O \tag{19}$$

2.   Rainout

As was mentioned in Section III, rainout can be an important physical removal process for polar compounds such as alcohols. However, little is known at this time about the reactions and how they might affect the atmospheric lifetimes of alcohols.

C.   TOXICITY

Lower molecular weight alcohols exhibit a range of toxicities. Methanol, also known as wood alcohol, causes mild inebriation followed in about 10-20 hours by unconsciousness and cardiac depression; death may follow. Sublethal exposure may lead to blindness. The symptoms of ethanol are well known—decreased inhibitions and CNS depression are the first symptoms, followed by stupor, coma, and death at higher doses. Ethanol can be absorbed through the lungs and symptoms of intoxication observed at 1000 ppm. Ethylene glycol, the anti-freeze/antiboiling formulation in most automotive cooling systems, stimulates the CNS and then depresses it; potentially fatal kidney damage can occur.

The toxicity of higher molecular weight alcohols range from relatively low to moderate. For example, 2-propanol ($CH_3CHOHCH_3$), or rubbing alcohol, is a food additive which can be an irritant and narcotic, but one with relatively low toxicity. Allyl alcohol ($CH_2=CHCH_2OH$) has

a pungent odor and is strongly irritating to eyes, mouth, and lungs. Deaths have been reported in laboratory animals but not humans (Reference 62). The following irritants—1-butanol ($CH_3(CH_2)_2CH_2OH$), 2-ethylhexanol ($CH_3(CH_2)_3CH(C_2H_5)CH_2OH$), and 1-pentanol ($CH_3(CH_2)_3CH_2OH$)—have limited toxicity due to low vapor pressure. Most other higher molecular weight alcohols are also considered to be moderately toxic by ingestion or skin contact (Reference 32).

Based on the toxicity of the non-halogenated alcohols, there is reason to believe that compounds containing bromine with acceptable toxicity could be found. Table 14 gives information on some alcohols having structural features that could be included in compounds of interest here. Where available, inhalation data have been given. In general, information for toxicity by intravenous and intraperitoneal routes has been omitted.

TABLE 14. TOXICITY AND SAFETY INFORMATION FOR SELECTED ALCOHOLS.

Compound	Formula	CAS No.	Observations[a]
2,2-bis(2-Bromoethyl)-1,3-propanediol	$CH_2OHC-(CH_2CH_2Br)_2CH_2OH$	3296-90-0	[BHI000] Little toxicity data available. Suspected carcinogen. HR = 3.
1-Bromoacetoxy-2-propanol	$CH_2BrC(O)O-CH_2CH_2(OH)CH_3$	4189-47-3	[BMS250] LD_{50} (rat, oral) = 664 mg/kg, LD_{50} (rabbit, skin) = 813 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
2-Bromoethanol	CH_2BrCH_2OH	540-51-2	[BNI500] TD_{LO} (mouse, oral) = 43 g/kg. Poison by intraperitoneal. Experimental neoplastigen, tumorigen. HR = 3.
2-Bromoethynyl-2-butanol	$CH_3CH_2C(C{\equiv}C-CH_2Br)(OH)CH_3$	2028-52-6	[BNK350] LD_{50} (mouse, oral) = 532 mg/kg. Moderately toxic by ingestion, other routes. HR = 2.
3-Bromopropanol	$CH_2BrCH_2CH_2OH$	627-18-9	[BNY750] Mutagenic data.
1,3-Dibromo-2-propanol	$CH_2BrCH(OH)-CH_2Br$	96-21-9	[DDR800] Poison by intraperitoneal. HR = 3.
2,3-Dibromo-1-propanol	$CH_2BrCHBrCH_2OH$	96-13-9	[DDS000] Poison by intraperitoneal. HR = 3.
1,3-Difluoro-2-propanol	$CH_2FCH_2CHF(OH)$	453-13-4	[DKI800] Poison by intravenous. HR = 3.
2-Fluoroethanol	CH_2FCH_2OH	371-62-0	[FIE000] LC_{50} (rat, inhalation, 10 min) = 200 mg/m^3, LC_{50} (mouse, inhalation, 10 min) = 1100 mg/m^3. Poison by inhalation, intraperitoneal, subcutaneous, intravenous. HR = 3.

TABLE 14. TOXICITY AND SAFETY INFORMATION FOR SELECTED ALCOHOLS (continued).

Compound	Formula	CAS No.	Observations[a]
2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-nonanol	$CHF_2(CF_2)_7CH_2OH$	376-18-1	[FIE000] LD_{LO} (rat, oral) = 4400 mg/kg. Poison by intraperitoneal. Mildly toxic by ingestion. HR = 3.
1,1,1,3,3,3-Hexafluoro-2-propanol	$CF_3CH(OH)CF_3$	920-66-1	[HDC500] LC_{LO} (rat, inhalation, 4 hr) = 3200 ppm, LD_{50} (mouse, oral) = 600 mg/kg. Poison by intravenous, intraperitoneal. Mildly toxic by inhalation. Severe eye irritant. HR = 3.
[b]Octafluoro-1-pentanol	$C_5H_3F_8OH$	39660-55-4	[OBS800] LC_{50} (mouse, inhalation, 2 hr) = 10,500 mg/m^3, LD_{50} (rat, oral) = 1110 mg/kg. Moderately toxic by ingestion, intraperitoneal. Mildly toxic by inhalation. HR = 2.
2,2,3,3,4,4,5,5-Octafluoro-1-pentanol	$CHF_2CF_2CF_2CF_2$-CH_2OH	355-80-6	[OBU000] LC_{LO} (rat, inhalation, 4 hr) = 2500 ppm. Mildly toxic by inhalation. HR = 1.
2,2,3,3,3-Pentafluoro-1,1-propanediol	$CF_3CF_2CH(OH)_2$	422-63-9	[PBE500] LD_{50} (mouse, oral) = 600 mg/kg. Moderately toxic by ingestion, intraperitoneal. HR = 2.
2,2,3,3,3-Pentafluoro-1-propanol	$CF_3CF_2CH_2OH$	422-05-9	[PBE500] LD_{LO} (rat, oral) = 2250 mg/kg. Moderately toxic by ingestion, intraperitoneal. HR = 2.
2,2,2-Trifluoro-1,1-ethanediol	$CF_3CH(OH)_2$	421-53-4	[TJZ000] LD_{50} (mouse, oral) = 600 mg/kg. Moderately toxic by ingestion, intraperitoneal, intravenous. HR = 2.

57

TABLE 14. TOXICITY AND SAFETY INFORMATION FOR SELECTED ALCOHOLS
(concluded).

Compound	Formula	CAS No.	Observations[a]
2,2,2-Trifluoroethanol	CF_3CH_2OH	75-89-8	[TKA350] LC_{50} (mouse, inhalation) = 2900 mg/m^3, LD_{50} (rat, oral) = 240 mg/kg, LD_{50} (rat, skin) = 1680 mg/kg. Poison by ingestion, intraperitoneal, intravenous. Moderately toxic by inhalation, skin contact. Severe skin, eye irritant. HR = 3.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.
[b]Isomer not specified.

SECTION IX

ETHERS

A.   CHEMISTRY

Ethers contain the group C-O-C. The structural formula for one very common cyclic

ether (tetrahydrofuran, C_4H_8O) is shown in Figure 12. The simplest ethers have the formula

R-O-R', where R and R' are alkyl groups. The alkyl groups can be halogen substituted to give,

for example, the perfluoroether (PFE) hexafluorodimethyl ether (CF_3OCF_3). Using the rationale

discussed earlier, the most promising compounds would be partially fluorinated ethers containing

hydrogen adjacent to the nitrogen atom (to enhance hydroxyl free radical abstraction) and

bromine to provide fire suppression. Compounds discussed in the following sections are

primarily the hydrofluoroethers (HFE) on which hydrobromofluoroethers (HBFEs) will be based.
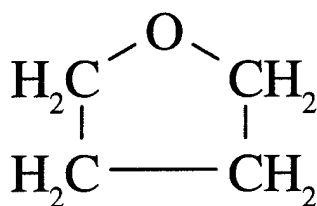
Figure 12. Tetrahydrofuran.

1.   Properties

A relatively large amount of work has gone into the perfluoroethers (PFE or FE)

as replacements for refrigerants and other ozone-depleting chemicals. Of greater interest here,

however, are the ethers that are only partially substituted by fluorine—the HFEs.

The NIST report cited earlier (Reference 49) lists several ethers for consideration

of model compounds for investigation. These compounds are listed in Table 15 with some name

changes and corrections. The physical properties are given in Table 16. Again, it must be

pointed out that these compounds were not listed as halon replacement candidates, but rather as

exploratory compounds for use in fire suppression studies.

TABLE 15. NIST EXPLORATORY LIST OF ETHERS.

Name	Formula	CAS No.
[a]1,1,3,3-Tetrafluorodimethyl ether	CF_2HOCF_2H	1691-17-4
[a]Pentafluorodimethyl ether	CF_2HOCF_3	3822-68-2
[a]2-Chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane	CF_2HOCF_2CHFCl	13838-16-9
[a]2-Chloro-2-(difluoromethoxy)-1,1,1-trifluoroethane	$CF_3CHClOCHF_2$	26775-46-7
[a]Perfluoro-2-butyltetrahydrofuran	$C_4F_9C_4F_7O$	335-36-4
Bis(bromodifluoromethyl) ether	CF_2BrOCF_2Br	Not available
Bromopentafluorodimethyl ether	CF_2BrOCF_3	Not available
2-Chloro-1,1,2-trifluoro-1-(bromodifluoromethoxy)ethane	CF_2BrOCF_2CHFCl	Not available
Octafluorotetrahydrofuran	C_4F_8O	773-14-8
3-Bromoheptafluorotetrahydrofuran	C_4F_7BrO	Not available

[a]Commercially available.

TABLE 16. PROPERTIES OF ETHERS IN NIST EXPLORATORY LIST.

Formula	Boiling point, °C	Vapor pressure, atm at 298 K	Heat capacity, J/mol-K at 298 K	Heat of vaporization, kJ/mol at boiling point
CF_2HOCF_2H	2	[a]2	[a]92	[a]24.5
CF_2HOCF_3	-35	[a]7	[a]109	[a]21.2
CF_2HOCF_2CHFCl	56.5	0.29	[a]162	[a]29.4
$CF_3CHClOCHF_2$	48.5	0.32	[a]167	[a]28.7
$C_4F_9C_4F_7O$	103	[a]0.033	Not available	[a]33.5
CF_2BrOCF_2Br	[a]25	[a]1	[a]117	[a]26.7
CF_2BrOCF_3	[a]-30	[a]6	[a]104	[a]24.7
CF_2BrOCF_2CHFCl	[a]67	[a]0.2	[a]175	[a]30.3
C_4F_8O	[a]50	[a]0.33	[a]151	[a]28.8
C_4F_7BrO	[a]105	[a]0.03	[a]159	[a]33.7

[a]Estimated (Reference 49).

Two fluorinated materials announced as substitutes for ozone-depleting cleaning agents (Reference 63), are now known to be the HFEs: methyl perfluorobutyl ether ($C_4F_9OCH_3$) and ethyl perfluorobutyl ether ($C_4F_9OC_2H_5$). The compositions and properties are given in Table 17.[*] More recently, a number of additional HFEs have been announced (Table 18).[†] Heat capacities have been determined for gaseous (difluoromethoxy) difluoromethane (CHF_2OCHF_2, HFE-134), and 2-(difluoromethoxy)-1,1,1-trifluoroethane ($CF_3CH_2OCHF_2$, HFE-245fa1) (Reference 64). The heat capacity for HFE-134 can be fit with a polynomial expression $C_p/R = c_0 + c_1T + c_2T^2 + c_3T^3$, where T is the temperature in °C, R is the gas constant, $c_0 = 11.1251$, $c_1 = 0.032143$ °C^{-1}, $c_2 = -1.6095$ x 10^{-4} °C^{-2}, and $c_3 = 6.660$ x 10^{-7} °C^{-3}. The heat capacity of HFE-245fa1 can be fit with a similar 3-term polynomial with $c_0 = 15.201$, $c_1 = 0.04024$ °C^{-1}, and $c_2 = -5.46$ x 10^{-5} °C^{-2}. The critical temperatures and pressures of a large number of HFEs have been reported.[†]

2.   Synthetic Routes

Reactions 20-23 have been used to prepare partially fluorinated ethers (HFEs) for evaluation as ODS substitutes, although details of the preparation are unavailable.[‡]
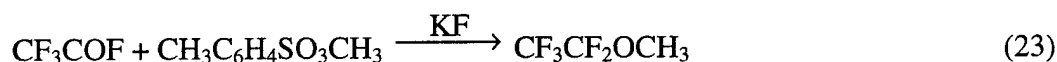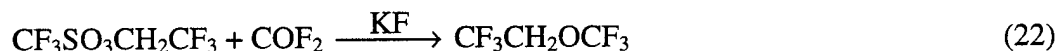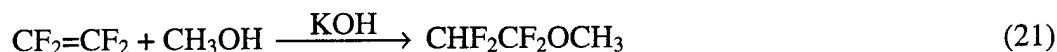
$$CF_3CH_2OH + CHClF_2 \xrightarrow{\text{KOH}} CF_3CH_2OCHF_2 \tag{20}$$

$$CF_2=CF_2 + CH_3OH \xrightarrow{\text{KOH}} CHF_2CF_2OCH_3 \tag{21}$$

$$CF_3SO_3CH_2CF_3 + COF_2 \xrightarrow{\text{KF}} CF_3CH_2OCF_3 \tag{22}$$

$$CF_3COF + CH_3C_6H_4SO_3CH_3 \xrightarrow{\text{KF}} CF_3CF_2OCH_3 \tag{23}$$

[*]Grenvell, M. W., Klin,, F. W., Owns, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

[†]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[‡]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

TABLE 17. HFEs ANNOUNCED AS CLEANING AGENT SUBSTITUTES.

Property	$C_4F_9OCH_3$	$C_4F_9OC_2H_5$
Halocarbon number	HFE-449s1	HFE-569sf2
Boiling point, °C	60	73
Melting point, °C	-135	-117
Flash point, °C	None	None
Flammability limits	None	None
Solubility of water at 25°C, ppm	95	92
Solubility in water at 25°C, ppm	<10	<10
Liquid density at 23°C, g/mL	1.50	1.43
Viscosity at 23°C, cp	0.4	0.4
Surface tension at 23°C, dynes/cm	13.6	13.6
Heat of vaporization, 23°C, kJ/kg	125.6	125.6
Specific heat, kJ/kg-K	1.172	1.214
ALC	>10%	>5%

3.   Flammability

Because they contain hydrogen as well as halogen, HFEs may be flammable or combustible. There are several different measures of flammability or combustibility. The flash point of a liquid is the temperature at which the vapor/air mixture just above the liquid is capable of momentarily supporting a propagating flame when a small gas pilot is swept across it. Of greater interest are the upper and lower flammability limits of a gas or liquid that could be vaporized. These limits define the minimum and maximum concentration percentages of the gas or vapor in a mixture with air or oxygen that can support a propagating flame. These values are determined through testing and reported on most flammable gases and liquids.

TABLE 18. PROPERTIES OF SOME HFEs.

Compound	Boiling point, °C	Viscosity at 23 °C, cp	Liquid density, g/mL	Surface tension at 23 °C, dynes/cm	Thermal conductivity, W/m-K	Specific heat, kJ/kg-K
CHF$_2$OCH$_2$CF$_3$	29.0	0.460	1.391	15.18	0.1053	1.368
CHF$_2$OCHFCF$_3$	23.3	0.426	1.454	13.16	0.0943	1.286
CH$_3$OCF$_2$CHF$_2$	37.2	0.448	1.288	16.97	0.1059	1.444
CH$_3$OCF$_2$CF$_2$CF$_3$	34.2	0.471	1.409	12.39	0.0753	1.246
CH$_3$OCF(CF$_3$)$_2$	29.9	0.463	1.420	11.86	0.0780	1.208
CF$_3$CH$_2$OCF$_2$CF$_3$	27.8	0.444	1.448	10.88	0.0801	1.269
CH$_3$OCF$_2$CF$_3$	5.6	a	a	a	a	a

[a]Not available.

63

It should be noted that there is a relationship between the flash point of a compound and the fluorine content defined as $N_F/(N_F + N_H)$, where N_F is the number of fluorine atoms and N_H is the number of hydrogen atoms (Table 19).* The limited data indicate that a fluorine content above 0.55 produces a nonflammable compound. The same trend and, possibly, approximately the same dividing point between flammable and nonflammable compounds is also observed for HFCs (Table 19). HFCs with a fluorine content of 0.5 or above are non-flammable (Table 20; Reference 65). The trend is more difficult to interpret, however, for HCFCs (Table 21) because of the addition of chlorine to the molecule. If one arranges compounds in order of both decreasing fluorine content and decreasing halogen content (defined as NX/(NX + NH), where NX is the number of halogen atoms and NH is the number of hydrogen atoms) one does, indeed, reach a point where flammability appears; however, the very limited data indicate that the point is much different than one would expect. Although one would predict that fluorine and chlorine should have equivalent suppression capabilities (or even that chlorine would be better), HCFC-222aa with a halogen content of 0.875 is observed to have a flash point (Reference 66).

It has been proposed that HFCs will be nonflammable if the number of carbon-fluorine bonds exceeds the total number of carbon-carbon and carbon-hydrogen bonds (Reference 67). This measure of potential flammability is most likely closely related to the halogen content ratio described earlier. For the compounds in Table 19, nonflammability is observed when the number of carbon-fluorine bonds exceeds or equals the total number of carbon-carbon and carbon-hydrogen bonds. Otherwise, the compounds are flammable. It has also been noted (Reference 68) that the flammability of compounds whose number of carbon-fluorine bonds nearly equals the number of carbon-carbon and carbon-hydrogen bonds is affected by the amount of water vapor in the air. For example, HFC-245ca (1,1,2,2,3-pentafluoropentane, $CHF_2CF_2CH_2F$), with equal numbers of bonds, was nonflammable using dry air or 5 liters of air with 25 microliters of water, but became flammable upon the addition of 70 microliters of water

---

*Grenvell, M. W., Klin,, F. W., Owns, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 19. FLASHPOINTS AND FLUORINE CONTENTS OF SOME HFEs.

Compound	Fluorine content, $N_F/(N_F + N_H)$	Flash point, °C	Number of C-F Bonds	Number of C-C plus C-H bonds
$CF_3CH_2OCF_2CF_3$	0.8	None	8	4
$CHF_2OCHFCF_3$	0.75	None	6	3
$CH_3OCF_2CF_2CF_2CF_3$	0.75	None	9	6
$CH_3OCF_2CF_2CF_3$	0.7	None	7	5
$CH_3OCF(CF_3)_2$	0.7	None	7	5
$CHF_2OCH_2CF_2CF_3$	0.7	None	7	5
$CF_3CH_2OCF_2CHF_2$	0.7	None	7	5
$CH_3OCF_2CF_3$	0.625	None	5	4
$CHF_2OCH_2CF_3$	0.625	None	5	4
$CHF_2OCF_2CH_2F$	0.625	None	5	4
$CH_3OCH(CF_3)_2$	0.6	None	6	6
$CF_3CH_2OCH_2CF_3$	0.6	None	6	6
$CH_3OCF_2CF_2CHF_2$	0.6	None	6	6
$CH_3OCF_2CHFCF_3$	0.6	None	6	6
$CHF_2OCH_2CF_2CHF_2$	0.6	None	6	6
$CHF_2CH_2OCF_2CHF_2$	0.6	None	6	6
$CF_3CH_2OCF_2CH_2F$	0.6	None	6	6
$CH_3CH_2OCF_2CF_2CF_2CF_3$	0.543	None	9	9
$CH_3OCF_2CHF_2$	0.5	<-20	4	5
$CH_3OCH_2CF_2CF_3$	0.5	-16.5	5	7

TABLE 20. FLASHPOINTS AND FLUORINE CONTENTS FOR HFCs.

Halocarbon No.	Formula	[a]CAS No.	Fluorine content, $N_F/(N_F + N_H)$	Flash point, °C
HFC-4-3-10mee	$CF_3CHFCHFCF_2CF_3$	142347-08-8	0.833	[b]none
HFC-245fa	$CF_3CH_2CF_2H$	460-73-1	0.625	[c]none
HFC-356mcf	$CF_3CF_2CH_2CH_2F$		0.6	[d]none
HFC-143	CH_2FCHF_2	430-66-0	0.5	[e]-84

[a]Chemical Abstracts Service Number.
[b]Merchant, A. N., "An Update on HFC-43-10mee as a Replacement for CFC-113," presented at the International CFC and Halon Alternatives Conference, Washington, DC, 24-26 October 1994.
[c]Bogdan, M., "Blowing Agents: Producer and User Perspective," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1996.
[d]Basu, R. S., "Hydrofluorocarbon (HFC) Solvent Alternative," presented at the International CFC and Halon Alternatives Conference, Washington, DC, 24-26 October 1994.
[e]Reference 66.

TABLE 21. FLASHPOINTS, FLUORINE, AND HALOGEN CONTENTS FOR HCFCs.

Halocarbon No.	Formula	[a]CAS No.	Fluorine content, $N_F/(N_F + N_H)$	Halogen content, $N_X/(N_X + N_X)$	Flash point, °C
HCFC-225ca	$CF_3CF_2CHCl_2$	422-56-0	[a]0.625	[b]0.875	none
HCFC-225cb	$CClF_2CF_2CHClF$	507-55-1	0.500	[b]0.875	none
HCFC-222aa	$CF_2ClCCl_2CHCl_2$	422-30-0	0.250	[c]0.875	-53.6 to -53.8
HCFC-21	$CHCl_2F$	75-43-4	0.250	[d]0.750	-22

[a]Chemical Abstracts Service Number.
[b]Morikawa, S., "Cleaning Agents; Producer Perspective," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1996.
[c]Reference 66.
[d]Reference 69.

in 5 liters of air. While any of these predictors of flammability is not absolute, ethers with a halogen to hydrogen plus halogen ratio of 0.5 or greater would appear to be nonflammable, and those with a ratio less than 0.5 may exhibit some degree of flammability. These rough guidelines can guide the search for replacements to candidates with little or no flammability, a prime requirement for any replacement.

Lower flammability limits (LFL) of several haloethers considered as anesthetics are reported in Table 22 (Reference 34).

TABLE 22. LOWER FLAMMABILITY LIMITS OF SOME HALOETHERS.

Compound	LFL, % by volume	
	Air	Oxygen
$CF_2CH_2OCH=CH_2$	4.4	4.0-4.5
$CH_2CH_2CH_2OCF_2CHClF$	2.59	2.33
$-CF_2CF_2CF_2CH_2OCH_2-$	4.46	3.67
CH_3OCF_2CHClF	6	5
$CF_3CH_2OCH_2CF_3$	20	7
$CH_3OCF_2CHCl_2$	7	5.4
$CF_3CH_2OCF_2CHF_2$	25	Not available

B. ENVIRONMENTAL CHARACTERISTICS

The atmospheric lifetimes of PFEs are very long, and there is little evidence that the presence of an oxygen atom (which would give a small increase in polarity) causes a significant decrease in atmospheric lifetime. On the other hand, the addition of hydrogen atoms makes hydrogen atom abstraction possible by hydroxyl free radicals. Moreover, the presence of an ether linkage increases the reaction rate. Insertion of an ether group alpha to the position from which hydrogen abstraction occurs should increase the rate constant by a factor of $e^{631/T}$. Moving a CF_3 group out of this position should increase the rate constant by an additional factor of $e^{771/T}$ (Reference 22). Thus, for $T = 265$ K, the rate constant should increase by a factor of $e^{1410/T} =$

$e^{5.32} = 204$. The rate constant for an HFE would, therefore, be approximately 200 times larger and the atmospheric lifetime would be approximately 1/100 of the value of the non-ether, but fluorinated, parent compound. Indeed, data for a number of ethers show rate constants approximately 10^2 larger than similar hydrocarbons (Reference 19).

Lifetimes reported for HFEs vary widely. For example, pentafluorodimethyl ether, CHF_2OCF_3 (HFE-125) and bis(difluoromethyl)ether, CHF_2OCHF_2 (HFE-134) are reported to have atmospheric lifetimes of 82 years and 8 years (Reference 10). The value for HFE-125 is particularly long. On the other hand, a recent report lists HFEs with atmospheric lifetimes as low as 0.3 years.[*,†] As expected, the atmospheric lifetimes decrease as the number of hydrogen atoms increase (Table 23).

C.   TOXICITY

Ethers have relatively low toxicities due to the low reactivity of the C–O–C functional group arising from the high strength of the C–O bond. Several volatile ethers can affect the CNS. However, flammability and the formation of explosive peroxides tend to be more serious problems than toxicity. Table 24 (Reference 49), Table 25,[‡] and Table 26 (Reference 56) indicate that most of the HFEs exhibit relatively low toxicities and are not mutagenetic. Table 27 contains general toxicity and safety information from Reference 32 on ethers with structural features related to those of interest in this project.

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[†]Grenvell, M. W., Klin,, F. W., Owns, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

[‡]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

TABLE 23. ATMOSPHERIC CHARACTERISTICS OF SOME HFEs.

Compound	[a,b]Lifetime, years	GWP based on CFC-11	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
$CH_3OCF_2CHF_2$	0.47	0.01	128	39	12
$CH_3OCF_2CF_2CF_3$	[c]6.4, 5.6	0.11	1514	485	151
$CH_3OCF(CF_3)_2$	[c]4.9, 4.3	0.08	1183	368	115
$CH_3OCF_2CF_3$	6.5	0.13	1936	622	194
$CF_3CH_2OCH_2CF_3$	0.50	0.012	174	53	17
$CF_3CH_2OCF_2CFH_2$	1.84	0.045	675	207	65
$CHF_2OCH_2CF_3$	4.71	0.13	1878	583	182
$CHF_2OCF_2CH_2F$	2.18	0.07	999	306	96
$CHF_2OCHFCF_3$	4.04	0.13	1901	586	183
$CHF_2OCH_2CF_2CF_3$	1.62	0.04	557	170	53
$CHF_2OCH(CF_3)_2$	3.77	0.08	1228	378	118
$CH_3CH_2OCF_2CF_3$	0.30	0.005	75	23	7
$CF_3CH_2OCF_2CHF_2$	1.62	0.04	577	176	55
$C_4F_9OCH_3$	5.5	0.08	d	330	d
$C_4F_9OC_2H_5$	1.2	0.02	d	70	d

[a] Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[b]The atmospheric lifetimes for all but the last two compounds were apparently determined from the rate constants for reaction with hydroxyl free radicals at 277 K with respect to methyl chloroform (CH_3CCl_3) scaled to a tropospheric lifetime of 6.6 years for CH_3CCl_3.

[c]Two values are reported for the atmospheric lifetime of these compounds.

[d]Not available.

69

TABLE 24. TOXICITY OF ETHERS IN NIST EXPLORATORY LIST.

Formula	[a]Hazard rating	[b]Toxicity comments
CF_2HOCF_2H	c	No toxicity data available.
CF_2HOCHF_3	c	No toxicity data available.
CF_2HOCF_2CHFCl	2	Used as an anesthetic under names enflurane and enthrane. Mildly toxic by inhalation, ingestion, and subcutaneous routes.
$CF_3CHClOCHF_2$	c	Used as an anesthetic under name isoflurane.
$C_4F_9C_4F_7O$	c	Used as blood substitute.
CF_2BrOCF_2Br	c	No toxicity data available.
CF_2BrOCF_3	c	No toxicity data available.
CF_2BrOCF_2CHFCl	c	No toxicity data available. The non-brominated version is an anesthetic known as enflurane.
C_5F_8O	c	No toxicity data available. The perfluorobutyl substituted compound is used as a blood substitute, and the toxicity of this compound may be acceptable.
C_4F_7BrO	c	No toxicity data available.

[a]Reference 32.
[b]Reference 49.
[c]Not available.

TABLE 25. TOXICITY OF HFEs.

Compound	[a,b]Acute oral LD$_{50}$, mg/kg	Acute inhalation LC$_{50}$, mg/L	[a,c]Mutagenicity, Ames test	Skin irritation, rabbit
CH$_3$OCH$_2$CH$_2$F	<30	0.5-2.0 mg/L	Negative	Not available
CH$_3$OCF$_2$CHF$_2$	>300	>20	Negative	Non-irritant
CHF$_2$OCF$_2$CH$_2$F	>300	>20	Negative	Non-irritant
CH$_3$OCF$_2$CF$_2$CF$_3$	>300	>20	Negative	Non-irritant
CHF$_2$OCH$_2$CF$_2$CF$_3$	>300	>20	Negative	Non-irritant
CH$_3$OCH(CF$_3$)$_2$	>300	>20	Negative	Non-irritant
CH$_3$CH$_2$OCF$_2$CHF$_2$	>300	>20	Negative	Slight irritant
CF$_3$CH$_2$OCF$_2$CHF$_2$	>300	>20	Negative	Non-irritant

[a] Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December, 1995.

[b]Rat, 2 doses. The authors of the paper cited consider an LD$_{50}$ < 30mg/kg to be toxic.

[c]Rat, 4-hour. The authors of the paper cited consider an LC$_{50}$ of 0.5-2.0 mg/L to be toxic.

TABLE 26. HFE TOXICITY EVALUATION.

Compound	Toxicity evaluation
CH$_3$CF(CF$_3$)$_2$	Acute inhalation, 3% for 4 hours: no observable effects Subacute inhalation, 6 hr/day for 7 days: NOAEL >2.0g/m^3
CH$_3$OCF$_2$CF$_3$	Acute inhalation, 3% for 4 hours: no observable effects Inhalation test, 28 days: NOAEL >20.0 g/m^3 Ames test: Negative Chromosome aberration: Negative
CH$_3$OCF$_2$CF$_2$CF$_3$	Acute inhalation, 3% for 4 hours: no observable effects Acute oral: LD$_{50}$ > 2 g/kg Ames test: Negative Subacute inhalation: 6 hr/day for 7 days: NOAEL 7.0 g/m^3

TABLE 27. TOXICITY AND SAFETY INFORMATION FOR SELECTED ETHERS.

Compound	Formula	CAS No.	Observations[a]
(2-Bromoethyl) ethyl ether	$CH_2BrCH_2OCH_2CH_3$	Not available	[BNK250] No toxicity data available. An insecticide. Dangerous fire hazard. Flash point = 5 °C.
2-Chloro-1,1,2-trifluoroethyl methyl ether	$CHClFCHF_2OCH_3$	425-87-6	[CLR000] LD_{50} (rat, oral) = 5130 mg/kg, LD_{50} (rabbit, skin) = 200 mg/kg. Poison by skin contact. Mildly toxic by ingestion. Severe eye irritant. HR = 3.
2,2-Dichloro-1,1-difluoroethyl methyl ether	$CHCl_2CHF_2OCH_3$	76-38-0	[DFA400] LC_{50} (rat, inhalation, 4 hr) = 123 g/m^3, LC_{50} (mouse, inhalation, 2 hr) = 118 g/m^3, LC_{50} (mammal, inhalation) = 34 g/m^3. Human poison by ingestion. Mildly toxic by inhalation. Eye irritant. HR = 3.
Heptafluoroisobutene methyl ether	$(CF_3)_2C=CFOCH_3$	360-53-2	[HAY500] LD_{50} (rat, oral) = 1070 mg/kg, LD_{50} (mouse, oral) = 1070 mg/kg. Poison by intraperitoneal, intravenous. Moderately toxic by ingestion. HR = 3.
Bis(pentafluoroethyl)-ether	$CF_3CF_2OCF_2CF_3$	358-21-4	[PCG750] LC_{50} (mouse, inhalation, 2 hr) = 177 g/m^3, LD_{50} (rat, oral) = 20 g/kg. Mildly toxic by ingestion, inhalation, intravenous. HR = 1.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.

SECTION X
AMINES

A.   CHEMISTRY

Amines are derivatives of ammonia (NH_3) and have the general formula NRR'R" where the nitrogen substituents are alkyl groups. Using the same rationale as described for the ethers, the present emphasis is primarily on partially fluorinated alkyl-substituted amines with at least one bromine atom. The compounds described below are primarily the hydrofluoramines (HFA) upon which the hydrobromofluoroethers (HBFA) would be based.
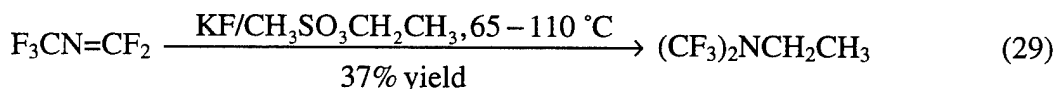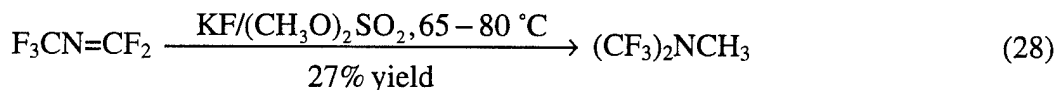
1.   Properties

Research from the National Industrial Research Institute of Nagoya has focused on fluoroalkylamines, with an emphasis on perfluoroalkyl derivatives, as fire suppressants (Reference 70). The inhibition effect of several bromine-free polyfluoroalkylamines including $N(CF_3CF_2)_3$, $N(CF_3)_2(CF_2CF_3)$, $N(CF_3)_2(CF_2CHF_2)$, and $N(CF_3)_2(CF=CF_2)$ on flame propagation has been measured by determining the laminar burning velocity for a mixture of 9.5 percent methane, 90.0 percent air, and 0.5 percent inhibitor, at an initial temperature of 298 K and a pressure of 760 Torr. All of the fluoroalkylamines inhibited flame propagation less than CF_3Br (Halon 1301), but more than HFC-227ea (CH_3CHFCF_3). Calculations showed that the inhibition effect of the fluoroalkylamines was caused not only by physical factors, but also by a chemical process in which fluorinated species capture combustion chain carriers (•H, •O, and •OH) to form stable HF molecules. The inhibition efficiencies of fluoroalkylamines were found to be higher than those of fluoroalkanes since fluoroalkylamine decomposes to reactive fluoroalkyl radicals in the lower temperature region of each flame (Reference 71). *Ab initio* molecular orbital calculations indicate that fire suppression by perfluoromethylamines is due, in part, to reactions of the trifluoromethyl radical, which can be easily released from perfluoroalkyl-amine by dissociation of C-N bonds (Reference 72). The proposed Reactions 24 to 26 are similar to those proposed for bromine in the case of the halons (Reference 54). It should be noted, however, that others have found no evidence for participation of •CF₃ in flame inhibition (Reference 73).

$$\bullet CF_3 + \bullet H \rightarrow CF_3H \tag{24}$$

$$CF_3H + \bullet H \rightarrow \bullet CF_3 + H_2 \tag{25}$$

$$CF_3H + \bullet OH \rightarrow \bullet CF_3 + H_2O \tag{26}$$

Recently several HFAs have been announced as replacements for refrigerants and solvents and are shown in Table 28.[*]

2. Synthetic Routes

Syntheses have been reported for preparation of HFAs, the parent compounds for HBFAs.[*] The reported synthesis begin with the preparation of the imine $CF_3N=CF_2$ in a two-step process using electrochemical fluorination (ECF) in the first step (Reaction 27). In Reaction 28, dimethyl- sulfate, $CH_3O\overset{O}{\underset{O}{S}}CH_3$ is used to alkylate the nitrogen, giving an iminium ion, $(CH_3)(CF_3)\overset{+}{N}=CF_2$, which further reacts with fluoride, F^-, to form the final product. This is a fairly well-known type of reaction used to form unsymmetrical amines. Reactions 29-31 accomplish the alkylation using alkyl methanesulfonates, $RO\overset{O}{\underset{O}{S}}CH_3$ having various alkyl groups, R. The alkyl methanesulfonates can be prepared by esterification of methanesulfonic acid, CH_3SO_2OH.
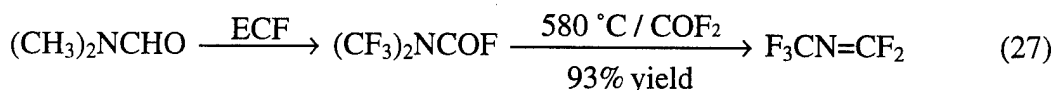
$$(CH_3)_2NCHO \xrightarrow{ECF} (CF_3)_2NCOF \xrightarrow[93\% \text{ yield}]{580\,^{\circ}C\,/\,COF_2} F_3CN=CF_2 \tag{27}$$

$$F_3CN=CF_2 \xrightarrow[27\% \text{ yield}]{KF/(CH_3O)_2SO_2,\,65-80\,^{\circ}C} (CF_3)_2NCH_3 \tag{28}$$

$$F_3CN=CF_2 \xrightarrow[37\% \text{ yield}]{KF/CH_3SO_3CH_2CH_3,\,65-110\,^{\circ}C} (CF_3)_2NCH_2CH_3 \tag{29}$$

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

TABLE 28. PROPERTIES OF SOME HFAs.

Compound	Boiling point, °C	Viscosity at 23 °C, cp	Liquid density, g/mL	Surface tension at 23 °C, dynes/cm	Thermal conductivity, W/m-K	Specific heat, kJ/kg-K	Flash point, °C	Fluorine content, $N_F/(N_F+N_H)$
$(CF_3)_2NCH_2CH_3$	33.3	0.41	1.129	12.55	0.0877	1.268	a	0.545
$(CH_3)_2NCH_2CF_3$	51.35	0.71	1.528	15.09	0.977	1.201	a	0.818
$(CF_3)_2NCH_3$	11-12	a	a	a	a	a	a	0.667
$(CF_3)_2NCH_2CH_3$	33-34	a	a	a	a	a	None	0.545
$(CF_3)_2NCH_2CF_2H$	50-52	a	a	a	a	a	None	0.727
$(CF_3)_2NCH_2CF_3$	38	a	a	a	a	a	a	0.818

aNot available.

$$F_3CN{=}CF_2 \xrightarrow[\text{59\% yield}]{\text{KF/CF}_3\text{SO}_3\text{CH}_2\text{CF}_2\text{H}, 60-65\,°C} (CF_3)_2NCH_2CF_2H \qquad (30)$$

$$F_3CN{=}CF_2 \xrightarrow[\text{51\% yield}]{\text{KF/CF}_3\text{SO}_3\text{CH}_2\text{CF}_3, 60-65\,°C} (CF_3)_2NCH_2CF_3 \qquad (31)$$
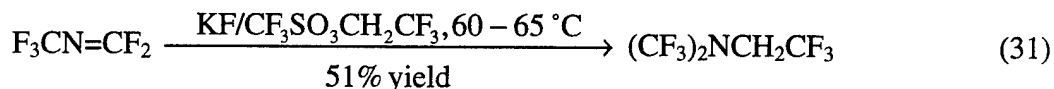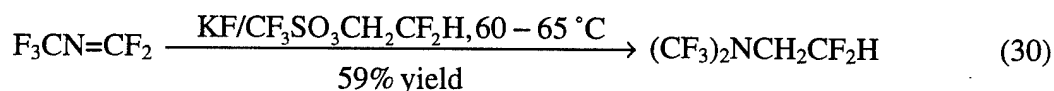
Perfluoropropanoic acid fluorides, which are precursors for preparation of HFAs, have been prepared by electochemical fluorination of methyl esters of 3-dialkylamino-substituted propionic acids (Reference 74). The following dialkylamino substituents were investigated: diethylamino, di-n-propylamino, di-n-butylamino, pyrrolidino, morpholino, and piperidino groups.

Of some interest here is the direct high-yield synthesis of nitrogen-containing perfluoroalkyl iodides by the reaction of corresponding perfluoroacid fluorides with lithium iodide (Reference 75).

B. ENVIRONMENTAL CHARACTERISTICS

When hydrogen atoms are present on both an amine alkyl group and on the nitrogen, C-H abstraction tends to occur in preference to or in competition with N-H abstraction. The presence of a nitrogen atom decreases the C-H bond strength. Thus, the bond energies for C-H in CH_4, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ are, respectively, 435, 391, 364, and 352 kJ/mol (104, 93.3, 87, and 84 kcal/mol) (Reference 76). As would be expected from these data, a nitrogen atom alpha to a C-H bond significantly increases the reaction rate constant for hydrogen abstraction by hydroxyl free radicals. This can be seen in the rate constants in Table 29 (Reference 19), which compares rate constants between amines and structurally similar hydrocarbons. For this limited set of data, the amine rate constants are 23 to 65 times large than the hydrocarbon rate constants. The calculated atmospheric lifetimes $t_{1/e}$ for the amines in Table 29 are less than 1 day based on their reactions with tropospheric hydroxyl free radicals only.

TABLE 29. RATE CONSTANTS FOR REACTIONS OF AMINES AND
HYDROCARBONS WITH HYDROXYL FREE RADICALS.

Compound	k_{OH}^1, cm^3/molecule-s	Compound	k_{OH}^1, cm^3/molecule-s
CH_3CH_3	3.40×10^{-13}	CH_3NH_2	2.20×10^{-11}
$(CH_3)_2CH_3$	1.37×10^{-12}	$(CH_3)_2NH$	6.54×10^{-11}
$(CH_3)_3CH$	2.67×10^{-12}	$(CH_3)_3N$	6.09×10^{-11}

Unfortunately, there are no reliable data for amines containing fluorine substitution. The atmospheric environmental parameters of some HFAs are given in Table 30;[*] however, the reliability of the numbers is uncertain. They may be estimates. The atmospheric lifetime for $(CH_3)_2NC_2F_6$ is unusually large, and it is probably in error. It may be that the compound is the fully fluorinated material $(CF_3)_2NC_2F_6$ or that the lifetime should have been 250 days rather than 250 years. The $t_{1/e}$ value for $(CF_3)_2NCH_3$ of 0.28 years is of particular interest since replacement of one of the fluorine atoms by bromine is likely to reduce this to about 0.028 years due to enhanced photolysis (Reference 54). A very small amount of data indicates that for bromine-containing compounds, each 10 years increase in atmospheric lifetime increases the ODP by approximately 2 (Reference 54). Thus, for an atmospheric lifetime of 0.028, $(CBrF_2)(CF_3)NCH_3$ would have an ODP of 0.006.

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

TABLE 30. ATMOSPHERIC CHARACTERISTICS OF SOME HFAs.

Compound	Lifetime, years	GWP based on CFC-11	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
$(CH_3)_2NC_2F_6$	[a] 250	4.3	4973	6527	5349
$(CF_3)_2NCHFCH_3$	2.98	0.06	930	287	90
$(CF_3)_2NCF_2CHF_2$	2.98	0.06	839	257	80
$(CF_3)_2NCH_3$	0.28	0.007	98	30	9
$(CF_3)_2NCF_2CF_2H$	2.10	0.01	141	43	13

[a]This value is highly suspect (see text).

C.   TOXICITY

The acute inhalation toxicity of some HFAs are give in Table 31.[*] In addition to these, the LC_{LO} for mouse inhalation has been reported as 500 mg/m^3 for 2,2,2-trifluoroethylamine $((CF_3CH_2)NH_2$, CAS No. = 753-90-2, SAX No. = TKA500) with a SAX Hazard Rating (HR) of 2 (Reference 32).

TABLE 31. ACUTE INHALATION TOXICITY OF HFAs.

Compound	LC_{50}, mg/L
[a]$(CF_3)_2NCH_3$	>20
[a]$(CF_3)_2NCF_2CF_2H$	>20
[a]$(CF_3)_2NCFHCF_3$	>20
[a]$(CF_3)_2NCH_2CF_3$	>20
[b]$(CF_3)_2NCH_2CF_2H$	>20
[b]$(CF_3)_2NCH_2CH_3$	>20

[a]3-Hour rat.
[b]4-Hour rat.

---

[*]Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

SECTION XI

CARBONYL COMPOUNDS

A.   CHEMISTRY

Carbonyl compounds contain a C=O group and include aldehydes, ketones, carboxylic acids, and esters (see Figure 13).
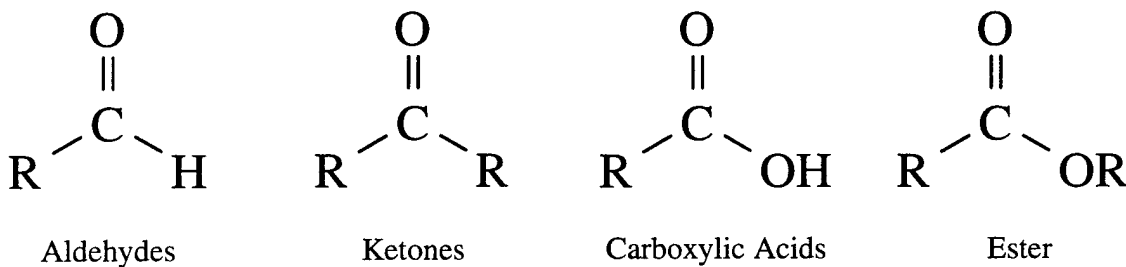
Figure 13. Carbonyl Compounds.

Aldehydes are reduced to form their respective alcohols; ketones are used as solvents. Carboxylic acids are used as food additives for flavor and preservation or used to reduce bases (formic acid). Esters are used as solvents, plasticizers, lacquers, soaps, and surfactants.

1.   Properties

The NIST exploratory list includes several carbonyl compounds (Reference 49). These carbonyls are listed in Table 32 with some very minor name changes. The physical properties are given in Table 33.

TABLE 32. NIST EXPLORATORY LIST OF CARBONYL COMPOUNDS.

Name	Formula	CAS No.
[a]Hexafluoroacetone	CF_3COCF_3	684-16-2
[a]Bis(perfluoroisopropyl)ketone	$(iC_3F_7)_2CO$	813-44-5
Methyltrifluoroacetate	CF_3COOCH_3	431-47-0
[a]3-Bromo-1,1,1-trifluoropropanone	CF_3COCH_2Br	431-35-6
Bromopentafluoroacetone	$CF_2BrCOCF_3$	815-23-6
(Bromomethyl)trifluoroacetate	CF_3COOCH_2Br	116478-92-4

[a]Commercially available.

TABLE 33. PROPERTIES OF NIST EXPLORATORY CARBONYLS.

Formula	Boiling point, °C	Vapor pressure, atm at 298 K	Heat capacity, J/mol-K at 298 K	Heat of vaporization, kJ/mol at boiling point
CF_3COCF_3	-26	6.65	118	20.9
$(iC_3F_7)_2CO$	73	[a]0.15	[a]280	[a]29.7
CF_3COOCH_3	44	[a]0.4	[a]113	[a]32
CF_3COCH_2Br	86	[a]0.08	[a]113	[a]32
$CF_2BrCOCF_3$	31	[a]0.9	[a]126	26.4
CF_3COOCH_2Br	[a]105	[a]0.03	[a]126	[a]33.7

[a]Estimated (Reference 49).

2.   Synthetic Routes

Perfluoroalkyl groups have been introduced into carbonyl compounds using a variety of zinc, calcium, manganese, magnesium, silver and lithium organometallic reagents (see Reference 57 for a brief survey with references).

An interesting route to a cyclopropene derivative containing a carboxyl or ester group is the reaction of a carbene :CFBr with vinyl nitrile, $CH_2=CH_2CN$ (Reference 77). The carbene is formed from phenyl(fluorodibromomethyl)mercury $((C_6H_5)Hg(CFBr_2))$, which can be

prepared from phenylmercuric chloride ($(C_6H_5)HgCl$) and dibromofluoromethane ($CHFBr_2$), in the presence of a strong base such as potassium t-butoxide ($(CH_3)_3COK$) (Reaction 32). Once formed, the cylopropyl nitrile can be hydrolyzed to give the carboxylic acid or converted to an ester by reaction with an alcohol.

$$CH_2=CH_2CN + (C_6H_5)Hg(CFBr_2) \rightarrow \quad \overset{\displaystyle CN}{\underset{F \quad Br}{\triangle}} \qquad (32)$$
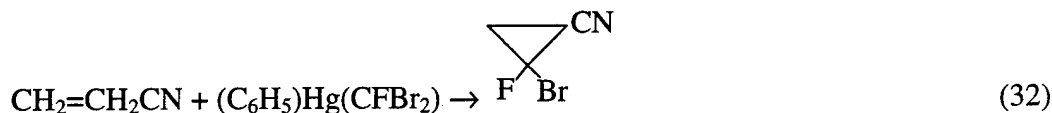
B. ENVIRONMENTAL CHARACTERISTICS

Carbonyl compounds can undergo photolysis and may also undergo physical removal, depending on the water solubility. Reaction with hydroxyl free radicals requires the presence of hydrogen atoms. Unfortunately, calculation of photolytic rates requires knowledge of the absorption cross sections as a function of wavelength, and, even then, the calculation is somewhat lengthy (Reference 53).

1. Aldehydes

The principal tropospheric removal mechanisms for aldehydes are photolysis and reaction with •OH free radicals (Reactions 4 and 33). Abstraction of a hydrogen atom from the R group can also occur if this group contains a hydrogen atom. In general, photolysis and hydrogen atom abstraction by atmospheric hydroxyl free radicals occur with comparable rates for aldehydes (Reference 24). Rate constants for reactions with hydroxyl free radicals and estimated quantum yields and absorption cross sections for photolysis indicate that aldehydes will have short atmospheric lifetimes, on the order of a few hours to approximately one month (References 10, 23, 24).

$$RC(O)H + hv \rightarrow \cdot R + \cdot C(O)H \qquad (33)$$

2. Carboxylic Acids

Lower molecular weight carboxylic acids are highly hydrophilic, and rainout is likely to be an exceedingly important removal process. The globally-averaged photodegradation

lifetime of trichloroacetic acid ($CCl_3C(O)OH$) is approximately 2 months, with a quantum yield of nearly 1 (Reference 78). Carboxylic acids have k_{OH}^1 values of about 1 to 2 x 10^{-12} cm^3/molecule-s (Reference 19) depending on the chain length (longer chains have more hydrogen atoms for abstraction). This corresponds to atmospheric lifetimes of 6 to 12 days. Replacement of hydrogen atoms with fluorine will increase these lifetimes. In spite of their attractive global environmental properties, however, carboxylic acids are relatively unattractive from a toxicological and physical property standpoint.

3.   Carboxylic Acid Halides and Carbonyl Halides

Carbonyl halides (COX_2) and carboxylic acid halides (RCOX), are highly susceptible to hydrolysis. These materials have hydrolysis lifetimes on the order of 1 to 2 months (Reference 20). They may also undergo significant photodecomposition. It is interesting that the carboxylic acid fluorides are much less susceptible to photodecomposition than are the chlorides. For example, acetyl fluoride ($CH_3C(O)F$) has an atmospheric photolysis lifetime of approximately 24 years and trifluoroacetyl fluoride ($CF_3C(O)F$) has a photolysis lifetime of approximately 1723 years (References 61). On the other hand, acid chlorides, such as trifluoroacetyl chloride ($CF_3C(O)Cl$) have photolysis lifetimes of a few days to a few months (References 61 and 79). Because of toxicity considerations, however, carbonyl halides and carboxylic acid halides (e.g., compounds containing a halogen atom directly bonded to a carbonyl carbon atom) are not suitable candidates as halon substitutes.

4.   Ketones

There is some evidence that free radicals alpha to carbonyl groups (Figure 14) may receive stabilization of 2.7 to 7 kcal/mole due to delocalization (Reference 25). The rate constants for reactions of non-halogenated ketones with hydroxyl free radicals are relatively large (Reference 19), and the atmospheric lifetimes will be on the order of days. In addition, these compounds undergo photolysis in the troposphere. The method of Wuebbles and Connell (Reference 15) used to estimate lifetimes due to hydrogen atom abstraction, however, shows that halogen substitution greatly increases the atmospheric lifetimes (Table 34). Thus, halogenated

ketones are suitable only if the photolytic lifetime is sufficiently short. Without absorption cross sections for compounds of interest, photolysis estimates cannot be made.
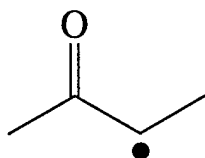

Figure 14. Free Radical Alpha to Carbonyl.

TABLE 34. ESTIMATED FIRST-ORDER RATE CONSTANTS FOR HYDROGEN ATOM ABSTRACTION AND ATMOSPHERIC LIFETIMES FOR SOME BROMOFLUOROKETONES.

Compound	k_{OH}^2 [•OH], s^{-1}	Lifetime, days
$CH_3C(O)CF_2Br$	2.9×10^{-8}	392
$CF_3CH_2C(O)CF_2Br$	1.2×10^{-8}	981
[a]$CH_3C(O)CH_2CF_2Br$	1.4×10^{-8}	795
[a]$CF_3CH_2C(O)CH_2CF_2Br$	4.6×10^{-9}	2521

[a]The CF_2Br group was approximated as CF_3 for the calculation on this compound.

5.   Esters

Fluorination of esters significantly decreases the rate constant for reaction with tropospheric hydroxyl free radicals. For example, methyl acetate has a rate constant at 296 K of 3.4×10^{-13} cm^3/molecule-s, while methyl trifluoroacetate has a rate constant of 5.2×10^{-14} at the same temperature (Reference 19). Using the method of Wuebbles and Connell (Reference 15) to estimate lifetimes due to hydrogen atom abstraction for the compounds $CBrF_2CH_2C(O)OCH_3$, $CBrF_2CF_2C(O)OCH_3$, and $CBrF_2CH_2C(O)OCF_3$ gives atmospheric lifetimes of 392, 654, and 981 days ($CBrF_2$ was approximated as CF_3). Thus, unless rainout and photolysis are significant, esters do not appear to be good compounds for constructing advanced streaming agents.

83

C. TOXICITY

Toxicities of carbonyl compounds from the NIST exploratory list are shown in Table 35 (Reference 49). Table 36 gives information on toxicology and safety for some carbonyl compounds structurally related to compounds of interest here (Reference 32). In this table, all available inhalation toxicity data are given; however, intraperitoneal and intravenous toxicity data are not presented.

TABLE 35. TOXICITY OF CARBONYL COMPOUNDS IN NIST EXPLORATORY LIST.

Formula	[a]Hazard rating	[b]Toxicity comments
CF_3COCF_3	3	[a]Moderately toxic by ingestion and a poisonous irritant to the skin, eyes, and mucous membranes.
$(iC_3F_7)_2CO$	c	No toxicity data available. Expected to be similar to CF_3COCF_3.
CF_3COOCH_3	c	No toxicity data available.
CF_3COCH_2Br	c	No toxicity data available. Expected to be similar to CF_3COCF_3.
CF_2BrOCF_3	c	No toxicity data available. Expected to be similar to other esters.
CF_3COOCH_2Br	c	No toxicity data available. Expected to be similar to other esters.

[a]Reference 32.
[b]Reference 49.
[c]Not available.

TABLE 36. TOXICITY AND SAFETY INFORMATION FOR SELECTED CARBONYL COMPOUNDS.

Compound	Formula	CAS No.	Observations[a]
1,2-Bis(bromoacetoxy)-ethane	$CH_2BrC(O)OCH_2$-$CH_2OC(O)CH_2Br$	3785-34-0	[BHD250] Poison by intraperitoneal, intravenous. HR = 3.
2-Bromoethanaldehyde	$CH_2BrC(O)H$	17157-48-1	[BMR000] Mutagenic data.
2-Bromoethanoic acid	$CH_2BrC(O)OH$	79-08-3	[BMR750] LC_{LO} (rat, inhalation, 30 min) = 114 g/m^3 (2.02%). Poison by ingestion, intraperitoneal, intravenous. Irritating, corrosive to skin, mucous membranes. HR = 3.
1-Bromoacetoxy-2-propanol	$CH_2BrC(O)O$-$CH_2CH_2(OH)CH_3$	4189-47-3	[BMS250] LD_{50} (rat, oral) = 664 mg/kg, LD_{50} (rabbit, skin) = 813 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
2-Bromo-2-propenal	$CH_2=CBrCHO$	14925-39-4	[BMT000] Mutagenic data.
2-Bromobutanoic acid	$CH_3CHBrCH_2$-$C(O)OH$	80-58-0	[BMY250] LD_{50} (mouse, oral) = 310 mg/kg. Poison by ingestion. HR = 3.
Bromo-2-propanone	$CH_2C(O)CH_3$	598-31-2	[BNZ000] LC_{LO} (human, inhalation, 10 min) = 572 ppm. Poisonous gas. Moderately toxic to humans by inhalation. HR = 3.
2-Bromopropionic acid	$CH_3CHBrC(O)OH$	598-72-1	[BOB000] LD_{50} (mouse, oral) = 250 mg/kg. Poison by ingestion. HR = 3.
3-Bromopropionic acid	$CH_2BrCH_2C(O)OH$	590-92-1	[BOB250] TD_{LO} (mouse, skin) = 4800 mg/kg. Moderately toxic by intraperitoneal. Experimental tumorigen, carcinogen. Mutagenic data. HR = 3.

TABLE 36. TOXICITY AND SAFETY INFORMATION FOR SELECTED
CARBONYL COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
Diethyl hexafluoropentanedioate	$(C_2H_5)OC(O)CF_2CF_2$ $-CF_2C(O)CO(C_2H_5)$	424-40-8	[DJK100] LC_{50} (rat, inhalation, 4 hr) = 1300 mg/m^3, LC_{50} (mouse, inhalation, 2 hr) = 10 g/m^3, LD_{50} (rat, oral) = 5 g/kg, LD_{50} (mouse, oral) = 4200 mg/kg. Moderately toxic by inhalation. Mildly toxic by ingestion. HR = 2.
Ethyl fluoroethanoate	$CH_3CH_2OC(O)CH_2F$	459-72-3	[EKG500] Poison by intraperitoneal. HR = 3.
Ethyl 2,2,3-trifluoropropanoate	$C_2H_5OC(O)CF_2CH_2F$	28781-86-4	[EQB500] No toxicity data. HR = 3.
Fluoroethanoic acid	$CH_2FC(O)OH$	144-49-0	[FIC000] LD_{50} (rat, oral) = 4,680 μg/kg, LD_{50} (mouse, oral) = 7 mg/kg. Poison by ingestion, subcutaneous, intraperitoneal, intravenous. Causes convulsions and ventricular fibrillation in human CNS. HR = 3.
2-Fluoroethyl fluoroethanoate	CH_2FCH_2- $OC(O)CH_2F$	459-99-4	[FIM000] LC_{50} (rat, inhalation, 10 min) = 200 mg/m^3, LC_{50} (mouse, inhalation, 10 min) = 450 μg/m^3. Poison by inhalation, subcutaneous, parenteral. HR = 3.
2-Fluoroethyl 4-fluorobutanoate	CH_2FCH_2- $OC(O)CH_2CH_2CH_2F$	371-29-9	[FIN000] LC_{50} (rat, inhalation, 10 min) = 200 mg/m^3, LC_{50} (mouse, inhalation, 10 min) = 73 mg/m^3. Poison by inhalation. HR = 3.

TABLE 36. TOXICITY AND SAFETY INFORMATION FOR SELECTED
CARBONYL COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
Heptafluorobutanoic acid	$C_4H_7C(O)OH$	375-22-4	[HAX500] Poison by intraperitoneal. Probable eye, skin, mucous membrane irritant. HR = 3.
Ethyl heptafluorobutanoate	$C_4H_7C(O)OC_2H_5$	356-27-4	[HAY000] Poison by intraperitoneal. HR = 3.
Hexafluoro-2-propanone	$CF_3C(O)CF_3$	684-16-2	[HCZ000] LC_{50} (rat, inhalation, 3 hr) = 275 ppm, LD_{LO} (rat, oral) = 191 mg/kg. Poison by ingestion, possibly skin contact. Moderately toxic by inhalation. Poisonous irritant to skin, eyes, mucous membranes. Nonflammable. HR = 3.
Methyl bromoethanoate	$CH_3OC(O)CH_2Br$	96-32-2	[MHR250] Poison by intravenous route. HR = 3.
Methyl fluoroethanoate	$CH_3OC(O)CH_2F$	453-18-9	[MKD000] LC_{50} (rat, inhalation, 10 min) = 300 mg/m^3, LC_{50} (mouse, inhalation, 10 min) = 3200 mg/m^3, LD_{50} (rat, oral) = 3500 μg/kg, LD_{50} (mouse, oral) = 5 mg/kg. Poison by ingestion, inhalation, skin contact, subcutaneous, intramuscular, intraperitoneal, parenteral, intravenous. HR = 3.
Pentafluoropropanoic acid	$CF_3CF_2C(O)OH$	422-64-0	[PBF000] LD_{10} (rat, oral) = 750 mg/kg. Poison by intraperitoneal. Moderately toxic by ingestion. HR = 3.
Perfluorodecanoic acid	$CF_3(CF_2)_8C(O)OH$	335-76-2	[PCG725] Poison by intraperitoneal. Experimental reproductive effects. HR = 3.

TABLE 36. TOXICITY AND SAFETY INFORMATION FOR SELECTED CARBONYL COMPOUNDS (concluded).

Compound	Formula	CAS No.	Observations[a]
Methyl perfluoromethoxy-propanoate	$CF_3OCF_2CF_2$-$C(O)OCH_3$	356-69-4	[PCH275] LC_{50} (mouse, inhalation) = 22 g/m^3, LD_{50} (mouse, oral) = 8000 mg/kg. Moderately toxic by intraperitoneal. Mildly toxic by ingestion, inhalation. HR = 2.
Methyl perfluoropropanoate	$CF_3CF_2C(O)OCH_3$	356-69-4	[PCH350] LC_{50} (mouse, inhalation) = 23 g/m^3, LD_{50} (mouse, oral) = 7000 mg/kg. Moderately toxic by intraperitoneal. Mildly toxic by ingestion, inhalation. HR = 2.
Trifluoroethanoic acid	$CF_3C(O)OH$	76-05-1	[TKA250] LC_{50} (rat, inhalation) = 10 g/m^3, LC_{50} (mouse, inhalation) = 13,500 mg/m^3, LD_{50} (rat, oral) = 200 mg/kg. Poison by ingestion, intraperitoneal. Moderately toxic by intravenous. Mildly toxic by inhalation. Corrosive irritant to skin, eyes, mucous membrane. HR = 3.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.

1.   Aldehydes

Lower aldehydes attack exposed moist tissue, especially eyes and mucous membranes. Higher aldehydes penetrate deeper into the respiratory tract and affect the lungs. Many members of the family are mutagens, and all have anesthetic properties. For example, acetaldehyde (CH_3CHO) is an irritant and CNS narcotic, while acrolein (2-propenal

($CH_2=CHCHO$)) is toxic by all routes. Some higher aldehydes and aromatic aldehydes may exhibit much lower toxicity. Aldehydes are converted to organic acids in the liver.

2.   Ketones

Ketones can act as a narcotic and dissolve fat in the skin (e.g., acetone ($CH_3C(O)CH_3$), can act as neurotoxins (methyl-*n*-butylketone, $CH_3C(O)CH_2CH_2CH_2CH_3$), and have been suspect in neuropathic disorders (methylethylketone, $CH_3C(O)CH_2CH_3$).

3.   Carboxylic Acids

Carboxylic acids can be corrosive to tissue and are often relatively toxic orally and by skin contact. The presence of more than one carboxylic acid group per molecule, unsaturated bonds in the carbon skeleton, or the presence of a halogen atom group on an alpha carbon increases toxicity and corrosivity.

Acid halides, RC(O)X, hydrolyze readily to give the free carboxylic acid and toxic hydrogen halides (Reaction 34). For this reason, these highly corrosive and irritating compounds cannot be considered as halon substitutes.

$$RC(O)X + H_2O \rightarrow RC(O)OH + HX \tag{34}$$

4.   Esters

Esters are hydrolyzed in tissue. The toxicity of the esters is primarily that of the hydrolysis products. Since esters have high volatility, pulmonary effects are important, and they are asphyxiants and narcotics. Because they are solvents, they tend to dissolve body lipids. Some natural esters are non-toxic. Synthetic esters, however, may have high toxicity. In general, fluorinated esters have a lower toxicity than fluorinated ketones (Reference 32).

A.   CHEMISTRY

Bromine-containing aromatic compounds have been widely used as flame retardants for plastics (Reference 80); however, little, if any, consideration has been given to their use as fire extinguishants. Many of the bromoaromatics used as plastic flame retardants are solids with reactive groups (for polymerization) and include compounds such as tetrabromobisphenol A $(CH_3C(C_6H_2Br_2OH)_2CH_3)$, bis(tetrabromophthalamide) $((C_6HBr_2(CONH_2)_2)_2)$, and dibromostyrene $((C_6H_3Br_2)CH=CH_2)$.

The aromatics consist of cyclic compounds formally containing alternating single and double bonds. Excluding some relatively rare organic ions, the simplest aromatic molecule is benzene (C_6H_6). The structural formula for benzene (and other aromatics) can be written as two or more equivalent structures (e.g., structures I and II for benzene in Figure 15), none of which adequately represents the actual structure due to delocalization of the π electrons over the ring. Structure III in Figure 15 is a somewhat better representation for benzene. To simplify the drawings, the carbon and hydrogen atoms are often omitted (Figure 16).
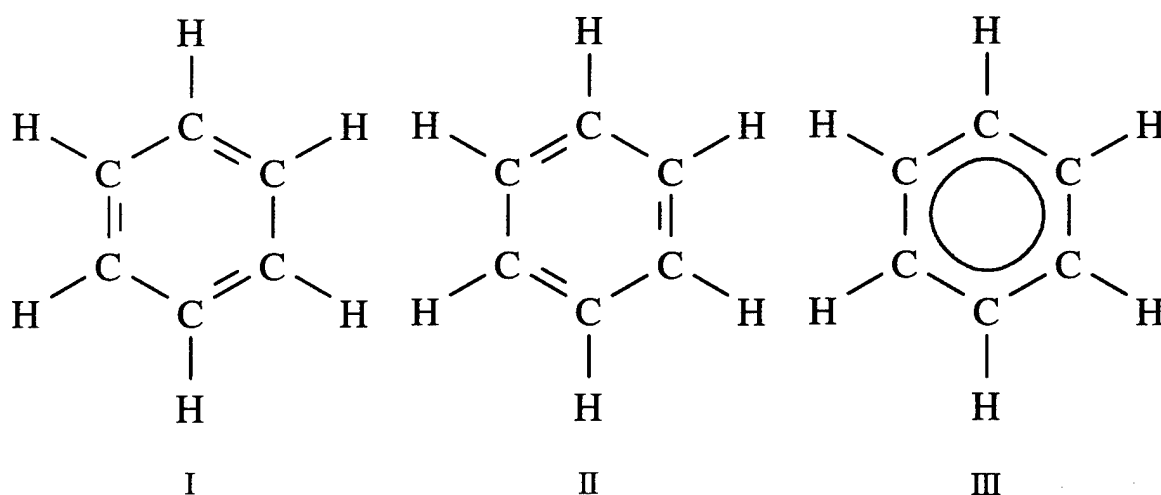
Figure 15. Graphical Structures for Benzene.
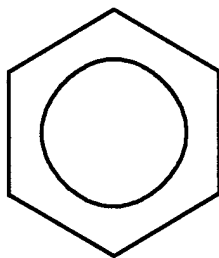
Figure 16. Simplified Graphical Representation for Benzene.

The rings can be fused to give polycyclic aromatic hydrocarbons (PAH) such as naphthalene or phenanthrene and can be linked to give compounds such as biphenyl (Figure 17). The rings can also contain atoms other than carbon, e.g., nitrogen, to give heterocyclic compounds such as pyridine (Figure 18). Consideration of volatility, toxicity, and environmental characteristics, however, indicates that simple derivatives of benzene are the most promising candidates for fire suppressants.

Naphthalene   Phenanthrene   Biphenyl

Figure 17. Aromatic Structures Containing Multiple Rings.

N

Figure 18. Pyridine.

1.   Properties

The NIST list of exploratory chemicals (Reference 49) contains one aromatic compound, perfluorotoluene ($CF_3C_6F_5$, CAS No. 434-64-0). The boiling point is 104 °C, and estimates have been made for the vapor pressure at 298 K (0.03 atmospheres), heat capacity at 298 K (207 J/mol-K), and heat of vaporization at the boiling point (34 kJ/mol).
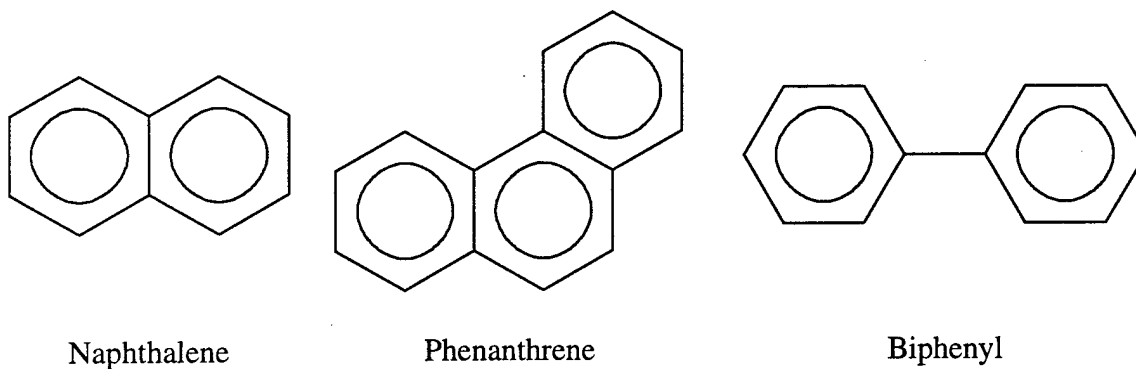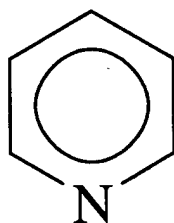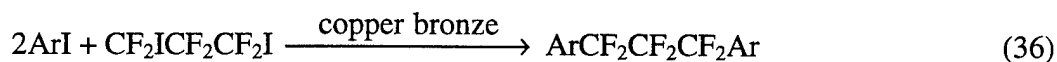
2.   Synthetic Routes

Trifluoromethylation of aromatic rings has been accomplished with a variety of reagents including trifluoromethylcopper (CF_3Cu), sodium trifluoroacetate ($NaOOCCF_3$), trifluoromethyl triflate, and bis(trifluoromethyl)mercury (CF_3HgCF_3) (see Reference 57 for a brief survey with references).

Fluoroalkyl groups (R_f) can be easily substituted into aromatic systems by reacting fluoroalkyliodides (R_fI) with aromatic iodides (ArI) in the presence of copper (Equation 35, Reference 51). The fluoroalkyl group, which can be partially fluorinated in some cases, attaches solely at the iodide position on the aromatic ring. Polar aprotic solvents such as dimethyl-formamide (DMF) and dimethylsulfoxide (DMSO) are used, and the reaction apparently involves the intermediate formation of fluoroalkylcopper compounds. Other groups such as phenyl, carboxylic ester, or free carboxyl groups may be present in the iodofluoroalkane, and a variety of substituents can be present on the aromatic (fluorine, chlorine, alkyl, alkoxy, carboxylic ester, nitro, free carboxyl, amino, and hydroxyl groups). Bromine, however, cannot be present and, in some reactions, can be used in place of the iodide substituent in the starting material. Two aryl groups can be coupled using a diiodocompound as shown in Equation 36 for 1,3-diiodo-1,1,2,2,3,3-hexafluoropropane ($CF_2ICF_2CF_2I$). This method has been used to prepare a number of trifluoromethyl, $-CF_3$, derivatives from CF_3I using a stainless steel reaction vessel with mechanical agitation to contain the gaseous trifluoromethyliodide (Reference 51).

$$R_fI + ArI \xrightarrow{\text{copper bronze}} ArR_f \qquad (35)$$

$$2ArI + CF_2ICF_2CF_2I \xrightarrow{\text{copper bronze}} ArCF_2CF_2CF_2Ar \qquad (36)$$

3.   Flammability

Lower flammability limits (LFL) of some halogenated aromatics that have been considered as anesthetics have been reported (Reference 34; Table 37).

TABLE 37. LOWER FLAMMABILITY LIMITS OF SOME HALOARENES.

| | LFL, % by volume | |
Compound	Air	Oxygen
o-$C_6H_4Cl_2$	2.2	not reported
C_6F_6	not reported	5-6
$C_6F_5CF_3$	<10	8.3
C_6F_5Br	not reported	5.8

B.   ENVIRONMENTAL CHARACTERISTICS

Hydroxyl free radicals can add to the aromatics as well as to other unsaturated compounds. At about room temperature most •OH radical reactions studied to date proceed by addition to the aromatic ring rather than by abstraction of a hydrogen atom. Rate constants for the reaction of hydroxyl free radicals with aromatic compounds are similar to those observed for the alkenes (Reference 19). Of particular interest is the 298 K rate constant of $k_{OH} = 2.2 \times 10^{-13}$ and approximately 3×10^{-12} cm^3/molecule-s observed for reactions with hexafluorobenzene (C_6F_6) and n-propylpentafluorobenzene ($CH_3CH_2CH_2C_6F_5$) (Reference 81). These compounds are closely related to some of the more promising tropodegradable aromatic candidates. The reaction rates for the nonfluorinated analogs are somewhat faster—$k_{OH} = 1.59 \times 10^{-12}$ and 7.8 x 10^{-12} cm^3/molecule-s for benzene and n-propylbenzene (Reference 81).[*] Thus, fluorination of the aromatic ring decreases the reaction rate with •OH. One can calculate the first order rate constants for the two fluorinated compounds as $k_1 = k_{OH}$ [•OH]. This gives $k_1 = 2.1 \times 10^{-7}$ s^{-1}

---

[*]In the case of the n-propyl derivative it is possible that some significant amount of reaction occurs by free-radical abstraction of hydrogen from the alkyl substituent.

93

($t_{1/e} = 1/k_1 = 54$ days) for hexafluorobenzene and $k_1 = 2.9 \times 10^{-6}$ s^{-1} ($t_{1/e} = 1/k_1 = 4$ days) for *n*-propylpentafluorobenzene.

One can use the method of Wuebbles and Connell (Reference 15) to estimate first-order rate constants and atmospheric lifetimes for a series of aromatic compounds of interest. The estimation method gives $k_1 = 8 \times 10^{-8}$ s^{-1}, ($t_{1/e} = 145$ days) for hexafluorobenzene and $k_1 = 3 \times 10^{-7}$ s^{-1}, ($t_{1/e} = 39$ days) for *n*-propylpentafluorobenzene. These rate constants are a little smaller than those determined from the experimental second-order rate constants above. For the *n*-propyl derivative, this may be due, in part, to the presence of some hydrogen atom abstraction from the alkyl group. Table 38 contains some estimations for other aromatic compounds having structures similar to those of interest as candidate fire suppressants. It is obvious from these values that aromatics have an excellent potential for environmental acceptability, even with bromine present.

C.   TOXICITY

Aromatic halocarbons have wide-ranging industrial use (Table 39), and, therefore, significant toxicological information is available for these compounds. Like the haloalkenes, however, most of those in use are chlorine-containing compounds, rather than the fluorine derivatives, which are of particular interest here. Of some interest are the various isomers of the chlorobenzotrifluorides.

Many of the aromatic halocarbons are irritants and can affect the respiratory system and liver. Table 40 gives some information on toxicity and safety of some aromatics structurally related to possible tropodegradable agents (References 32 and 33). Of particular interest is bromobenzene, which has been shown to cause liver damage in animal tests, although little information is available about this compound (Reference 56). Benzotrifluorides are under development as replacements for ozone-depleting solvents and are being considered for SNAP listing (Reference 82). The parent compound, (trifluoromethyl)benzene (trifluorotoluene, $C_6H_5CF_3$) is said to be "Highly toxic by inhalation. Flammable, dangerous fire risk" (Reference 83). The 4-hour rat LC$_{50}$ of 70,810 mg/m^3 (Table 40) corresponds to a concentration of 1.18 percent. The chloro derivatives are also said to be toxic and flammable.

TABLE 38. ESTIMATED FIRST-ORDER RATE CONSTANTS AND ATMOSPHERIC LIFETIMES FOR SOME BROMOFLUOROARENES.
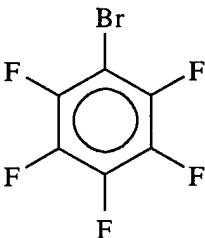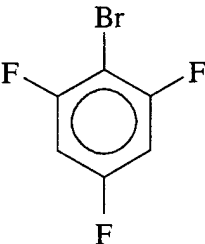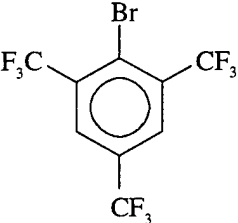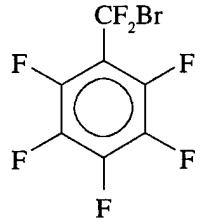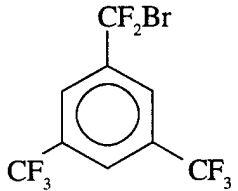
Structure	Chemical name	k_1, sec^{-1}	Lifetime, days
	Bromopentafluorobenzene	8.0×10^{-8}	145
	1-Bromo-2,4,6-trifluorobenzene	9.8×10^{-8}	117
	1-Bromo-2,4,6-tris(trifluoromethyl)benzene	4.4×10^{-6}	3
	(Bromodifluoromethyl)-pentafluorobenzene	3.2×10^{-6}	4
	1-(Bromodifluoromethyl)-3,5-bis(trifluoromethyl)benzene	4.9×10^{-6}	2.4

95

TABLE 39. AROMATIC HALOCARBONS USED IN INDUSTRY.
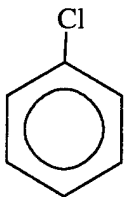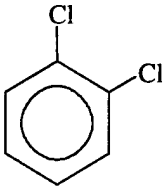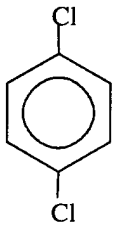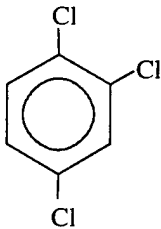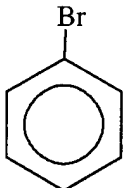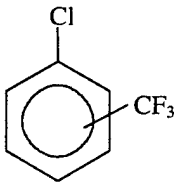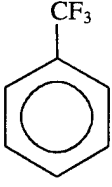
Structure	Chemical name	Application
	Chlorobenzene (phenyl chloride)	Solvent, heat transfer fluid, fumigant, intermediate
	1,2-Dichlorobenzene	Solvent, fumigant, intermediate
	1,4-Dichlorobenzene	Moth repellent, germicide
	1,2,4-Trichlorobenzene	Solvent, lubricant, dielectric, intermediate
	Bromobenzene	Solvent, motor oil additive
	Chloro(trifluoromethyl)benzenes, chlorobenzotrifluorides	Solvents, intermediates, dielectric fluids
	Trifluoromethylbenzene (benzotrifluoride)	Solvent, intermediate

TABLE 40. TOXICOLOGICAL AND SAFETY INFORMATION FOR AROMATICS RELATED TO POSSIBLE TROPODEGRADABLE CANDIDATES.

Compound	Formula	CAS No.	Observations[a]
(Trifluoromethyl)benzene	$C_6H_5CF_3$	98-08-8	[BDH500] LC_{50} (rat, inhalation, 4 hr) = 70,810 mg/m^3, LC_{50} (mouse, inhalation, 2 hr) = 92,240 mg/m^3, LD_{50} (rat, oral) = 15,000 mg/kg, LD_{50} (mouse, oral) = 10,000 mg/kg. HR = 3.
(Bromomethyl)benzene	$C_6H_5CH_2Br$	100-39-0	[BEC000] Intensely irritating, corrosive to skin, eyes, mucous membrane. Large doses cause CNS depression. Lachrymator. HR = 2.
Bis(4-bromophenyl)ether	$BrC_6H_4-O-C_6H_4Br$	2050-47-7	[BHJ000] Poison by intraperitoneal. HR = 3.
Bis(trifluoromethyl)-benzene	$C_6H_4(CF_3)_2$	402-31-3	[BLO270] No toxicity data.
2-Bromo-(trifluoromethyl)benzene	$BrC_6H_4(CF_3)$	392-83-6	[BOJ750] LD_{50} (rat, oral) = 2720 mg/kg. Moderately toxic by ingestion. Skin, eye irritant.
3-Bromo-(trifluoromethyl)benzene	$BrC_6H_4(CF_3)$	401-78-5	[BOJ500] LD_{50} (rat, oral) = 2870 mg/kg. Moderately toxic by ingestion. Skin, eye irritant.
4-Chloro-(trifluoromethyl)benzene	$ClC_6H_4(CF_3)$	98-56-6	[CEM825] LC_{50} (rat, inhalation, 4 hr) = 22 g/m^3 (0.30%), LC_{50} (mouse, inhalation) = 20 g/m^3 (0.27%), LD_{50} (rat, oral) = 13 g/kg, LD_{50} (mouse, oral) = 11,500 mg/kg. Mildly toxic by ingestion, inhalation. Human mutagenic data. Flammable. HR = 1.
1,3-Difluorobenzene	$C_6H_4F_2$	372-18-9	[DKF800] Very dangerous fire hazard. Flash point < 32 °C. HR = 3
1,4-Difluorobenzene	$C_6H_4F_2$	540-36-3	[DKG000] Very dangerous fire hazard. Flash point = 23 °C. HR = 3

TABLE 40. TOXICOLOGICAL AND SAFETY INFORMATION FOR AROMATICS
RELATED TO POSSIBLE TROPODEGRADABLE CANDIDATES (concluded).

Compound	Formula	CAS No.	Observations[a]
[b]Ethyldibromobenzene	$C_6H_3Br_2(C_2H_5)$	30812-87-4	[EHY000] LC_{LO} (rabbit, inhalation, 7 hr) = 731 mg/m^3 (0.30%), LD_{LO} (rat, oral) = 12,283 g/kg, LD_{LO} (rabbit, oral) = 5,536 mg/kg. Moderately toxic by ingestion, inhalation. HR = 2.
Fluorobenzene	C_6H_5F	462-06-6	[FGA000] LC_{50} (rat, inhalation) = 26,908 mg/m^3 (0.68%), LC_{50} (mouse, inhalation, 2 hr) = 45 g/m^3 (1.1%), LD_{50} (rat, oral) = 4399 mg/kg. Mildly toxic by ingestion, inhalation. Dangerous fire hazard. HR = 2.
1-Fluoro-2-bromobenzene	C_6H_4BrF	1072-85-1	[FGX000] LD_{50} (rat, oral) = 1850 mg/kg. Moderately toxic by ingestion. Skin, eye irritant. HR = 2.
1-Fluoro-3-bromobenzene	C_6H_4BrF	1073-06-9	[FGY000] LD_{50} (rat, oral) = 670 mg/kg. Moderately toxic by ingestion. Skin, eye irritant. HR = 2.
Hexafluorobenzene	C_6F_6	392-56-3	[HDB000] LC_{50} (mouse, inhalation, 2 hr) = 95 g/m^2. Mildly toxic by inhalation. Dangerous fire hazard. Flash point = 50 °F. HR = 3.
Perfluorotoluene	$C_6F_5CF_3$	434-64-0	[PCH500] LC_{LO} (mouse, inhalation, 10 min) = 5000 ppm. Mildly toxic by inhalation. HR = 1.

[a]The SAX Number (Reference 32) is given in brackets followed by information from that reference; the RTECS Number (Reference 33) is given in braces, again followed by information from that source. "HR" denotes the SAX Hazard Rating.
[b]Isomer not specified.

Perfluorotoluene ($CF_3C_6F_5$) has been investigated as an anesthetic, and it is reported to be mildly toxic with delayed death at levels as low as 0.5 to 0.9 percent (Reference 84). Hexafluorobenzene (C_6F_6) (Reference 85), and pentafluorobenzene (C_6HF_5) (Reference 84), have both been reported as anesthetics with relatively low toxicities. Of great interest is that bromopentafluorobenzene (C_6BrF_5) shows no anesthetic effects and has a low toxicity.

SECTION XIII
RESULTS AND CONCLUSIONS

This report has identified eight different classes of tropodegradable compounds. The chemistry of each class was described, and environmental and toxicological screening undertaken. The following is a brief recap of each class:

1. <u>Iodides</u>. CF_3I is a promising replacement for Halon 1301 in unoccupied areas. Higher molecular weight fluorinated compounds may exhibit unacceptable toxicity for any application.

2. <u>Bromoalkanes</u>. Bromoalkanes may have problems with flammability, toxicity, and ODP. 1-Bromopropane shows promise.

3. <u>Bromoalkenes</u>. Bromoalkenes have extremely low atmospheric lifetimes, but little is known of the toxicity of fluoroalkenes and bromofluoroalkenes. Bromine- and chlorine-substituted ethenes, propenes, and butenes show decreased irritation, tissue damage, and toxicity but increased anesthetic potency compared to their saturated analogs.

4. <u>Alcohols</u>. Some higher-molecular weight alcohols exhibit low toxicity, and there is reason to believe that alcohols containing bromine could be found with acceptable toxicity.

5. <u>Ethers</u>. Ethers may be flammable if the number of C-C bonds plus the number of C-H bonds approaches the number of C-F bonds. In general, ethers have long lifetimes, although the lifetimes of some HFEs may be as low as 0.3 years. The addition of bromine will lower the lifetimes. The reported toxicities tend to be low.

6. <u>Amines</u>. Hydrofluoroamines have relatively low atmospheric lifetimes. There is limited toxicity information, although it appears that amines of acceptable toxicity could be found.

7. <u>Carbonyl Compounds</u>.
   Aldehydes. Aldehydes exhibit short atmospheric lifetimes, but have potentially high toxicity, although higher aldehydes and aromatic aldehydes may exhibit low toxicity.

100

Carboxylic Acids. While carboxylic acids are expected to have short atmospheric lifetimes, toxicological and physical properties rule out this class as a replacement.

Carboxylic Acid Halides and Carbonyl Halides. High toxicity of this class rules out its use as a replacement.

Ketones. Little data have been found on the ketones.

Esters. Esters have long estimated atmospheric lifetimes. They may also exhibit poor toxicological performance.

8. <u>Aromatics</u>. Aromatics have potentially low atmospheric lifetimes. Some compounds may also be fairly non-toxic, with bromopentafluorobenzene (C_6BrF_5) falling into that category.

Table 41 presents those tropodegradable compounds most likely to have the properties needed for a halon replacement. This list is subject to change depending on the results of further study. Note that these are optimal from preliminary considerations of structural features. Availability may be an equally important determining factor.

TABLE 41. MOST PROMISING TROPODEGRADABLE CANDIDATES.

Formula	Name	CAS No.
$CH_2=CHCF_2Br$	1-bromo-1,1-difluoro-1-propene	420-90-6
CF_2BrCH_2OH	1-bromo-1,1-difluoro-2-ethanol	
$CF_2H-O-CFHBr$	(difluoromethyl)(bromofluoromethyl)ether	
$CF_3CH_2-O-CH_2CF_2Br$	(2,2,2-trifluoroethyl)(2-bromo-2,2-difluoroethyl)ether	
$(CBrF_2)(CHF_2)_2N$	(bromodifluoromethyl)bis(difluoromethyl)amine	
$(CBrF_2)(CF_3)(CH_3)N$	(bromodifluoromethyl)(trifluoromethyl)methylamine	
C_6F_5Br	bromopentafluorobenzene	344-04-7
$C_6F_4Br_2$	dibromotetrafluorobenzene	27134-02-7; 1,2 isomer: 827-08-7; 1,3 isomer: 1559-87-1; 1,4 isomer: 17823-46-0
$C_6F_5CBrF_2$	(bromodifluoromethyl)pentafluorobenzene	35523-39-8
$C_6F_5CBrF_2$	bromoheptafluorotoluene	113601-46-0 2-bromo: 66820-64-2 3-bromo: 5360-80-5 4-bromo: 17823-46-0

SECTION XIV

RECOMMENDATIONS

Much of the groundwork for tropodegradable compounds has been laid. An extensive assessment and prediction of atmospheric lifetimes and ozone depletion potentials of the various families of tropodegradable agents has been reported here. Continuation studies in four areas are needed: (1) a thorough assessment of manufacturability and synthetic pathways for specific proposed compounds; (2) detailed toxicological assessment for the various compounds; (3) determination of emissions during extinguishment and assessment of toxicity of gases emitted; and (4) completion of fire extinguishment testing with a determination of extinguishment mechanisms and structural features enhancing extinguishment. Each of these areas is briefly discussed below.

1.   The manufacturability of promising compounds, such as those in Table 41, must be further assessed. Contacts have been made with some potential manufacturers, and further discussions are needed concerning synthetic pathways and production viability.

2.   The experimental toxicity of selected compounds, with an emphasis on those in Table 41, should be determined. Little or no toxicity information is available for any of these compounds. The cost for LC_{50} or LC_{LO} testing is expected to be approximately \$15,000 per compound. Note, however, that cardiac sensitization testing will be needed on final candidates. The cost of such testing is about \$35,000 to \$50,000 per compound.

3.   Testing is needed to characterize the emissions given off by tropodegradable candidates during fire extinguishment and contact with hot metal surfaces. Once emission components have been identified, the risk from toxicity of the emissions must be determined.

4.   Although a large amount of work has been performed on standard aliphatic halocarbons as extinguishing agents, little has been done on aromatics, alkyls, ethers, and amines. It is not unlikely that the extinguishment mechanisms for these compounds will differ significantly from the typical halocarbons and, for that matter, from each other.

REFERENCES

1. Brown, J. A., Jacobson, E., Dvorak, L. E., Gibson, J., Gupta, A., Metchis, K., Mossel, J. W., Simpson, T., Speitel, L. C., Tapscott, R. E., and Tetla, R. A., *Chemical Options to Halons for Aircraft Use*, DOT/FAA/CT-95/9, U.S. Department of Transportation, Federal Aviation Agency, Atlantic City, New Jersey, February 1995.

2. Skaggs, S. R., and Tapscott, R. E., *Advanced Streaming Agent Program: Candidate Survey*, Final Report, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, December 1994.

3. Tapscott, R. E., Moore, T. A., Kaizerman, J. A., Kibert, C. J., and Tetla, R. A., "Advanced Agent Halon Substitutes," *Proceedings, International CFC and Halon Alternatives Conference*, Washington, DC, pp. 644-648, 23-25 October 1995.

4. Tapscott, R. E., "Second-Generation Replacements for Halon," *Proceedings, First International Conference on Fire Suppression Research*, Stockholm and Borås, Sweden, pp. 327-335, 5-8 May 1992.

5. Tapscott, R. E., Heinonen, E. W., and Brabson, G. D., *Advanced Agent Identification and Preliminary Assessment*, WL-TR-96-XX, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, April 1996. NMERI 95/38/32350 (Draft)

6. Brown, J. A., Jacobson, E., Dvorak, L. E., Gibson, J., Gupta, A., Metchis, K., Mossel, J. W., Simpson, T., Speitel, L. C., Tapscott, R. E., and Tetla, R. A., *Chemical Options to Halons for Aircraft Use*, DOT/FAA/CT-95/9, U.S. Department of Transportation, Federal Aviation Agency, Atlantic City New Jersey, Task Group 6, International Halon Replacement Working Group, Federal Aviation Administration, February 1995.

7. "Ozone Depletion: 20 Years After the Alarm," *Chemical & Engineering News*, pp. 8-13, 15 August, 1994.

8. *Climate Change: The IPCC Scientific Assessment*, Intergovernmental Panel on Climate Change, 1994.

9. *Radiative Forcing to Climate Change: The 1994 Report of the Scientific Assessment Working Group of IPCC*, Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom, 1994.

10. *Scientific Assessment of Ozone Depletion: 1994*, Report # 37, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, United Nations Environment Programme, and World Meteorological Organization, February 1995.

11. Lesclaux, R., Caralp, F., Lightfoot, P. D., Danis, F., and Catoire, V, "Kinetics and Mechanisms of Reactions of Chloromethyl and Chloromethylperoxy Radicals," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 52-57.

12. Batt, L., Khan, M. A., Mitchell, T. J., Stewart, P. H., and Mathews, S., "Cl Haloalkyl-peroxy Radicals - Thermochemistry and Kinetic Spectroscopy," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, pp. 58-66, Dublin, Ireland, 14-16 May 1991.

13. Cohen, N., *Structure-Reactivity Relationships for Predicting Environmentally Hazardous Chemicals*, EPA/600/3-86/072, Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina, prepared by the Aerospace Corporation, El Segundo, California, December 1986.

14. Prinn, R., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E., and Simmonds, P. G., "Atmospheric Trends and Lifetime of CH_3CCl_3 and Global OH Concentrations," *Science*, Vol. 269, No. 5221, pp. 187-192, 1995.

15. Wuebbles, D. J., and Connell, P. S., *A Screening Methodology for Assessing the Potential Impact of Surface Releases of Chlorinated Halocarbons on Stratospheric Ozone*, UCID-19233, Lawrence Livermore Laboratory, Livermore, California, November 1981.

16. Bednarek, G., Brown, A. C., Canosa-Mas, C. E., Dessent, C., Kinnison, D. J., Parr, A. D., and Wayne, R. P., "Investigation of Reaction Pathways of Halogenated Hydrocarbons in the Troposphere," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 1-8.

17. Güsten, H., Klasinc, L., and Maric, D., "Prediction of the Abiotic Degradability of Organic Compounds in the Troposphere," *Journal of Atmospheric Chemistry*, Vol. 2, pp. 83-93, 1984.

18. Atkinson, R., "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical With Organic Compounds Under Atmospheric Conditions," *Chemical Review*, Vol. 85, pp. 69-201, 1985.

19. Atkinson, R., *Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds*, Journal of Physical and Chemical Reference Data, Monograph No. 1, American Chemical Society, Washington, DC, and American Institute of Physics, 1989.

20. *Scientific Assessment of Stratospheric Ozone: 1989, Volume II , Appendix: AFEAS Report*, WMO Global Ozone Research and Monitoring Project - Report 20, National Aeronautics and Space Administration, UK Department of the Environment, National Oceanic and Atmospheric Administration, UN Environment Program, World Meteorological Organization, Alternative Fluorocarbon Environmental Acceptability Study (AFEAS), 1989.

21. Heicklen, J., "The Correlation of Rate Coefficients for H-Atom Abstraction by HO Radicals with C—H Bond Dissociation Enthalpies," *International Journal of Chemical Kinetics*, Vol. 13, pp. 651-665, 1981.

22. Atkinson, R., "Estimations of OH Radical Rate Constants from H-Atom Abstraction from C-H and O-H Bonds Over the Temperature Range 250-1000 K," *International Journal of Chemical Kinetics*, Vol. 18, pp. 555-568, 1986.

23. C. Balestra-Garcia, G. Le Bras, G. Poulet, and H. Mac Leod, "Kinetic Study of the Reactions OH + Mono-, Di-, Tri-chloroacetaldehyde and Acetaldehyde," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 31-39.

24. Scollard, D., Corrigan, M., Sidebottom, H., and Treacy, J., "Kinetics and Mechanisms for the Oxidation of Halogenated Aldehydes," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 40-51.

25. Egger, K. W., and Cocks, A. T., "Homopolar and Heteropolar Bond Dissociation Energies and Heats of Formation of Radicals and Ions in the Gas Phase II. The Relationship between Structure and Bond Dissociation in Organic Molecules," *Helvetica Chimica Acta*, Vol. 56, No. 5, pp. 1537-1552, 1973.

26. Worsnop, D. R., Robinson, G. N., Zahniser, M. S., Kolb, C. E., Duan, S. X., DeBruyn, W., Shi, X., and Davidovitx, P., "Heterogeneous Chemistry of Alternate CFC Oxidation Intermediates," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 132-137.

27. Butler, R., and Snelson, A., "Kinetics of the Homogeneous Gas Phase Hydrolysis of CCl_3COCl, CCl_2HCOCl, $CH_2ClCOCl$, and $COCl_2$," *Journal of the Air Pollution Control Association*, Vol. 29, pp. 833-837, 1979.

105

28. Rodriquez, J. M., Ko, M. K. W., Sze, N. D., and Heisey, C. W., "Model Assessments of Concentrations of Tri-Fluoro Acetic Acid in Rainwater from Degradation of HCFC/HFCs," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere,* Dublin, Ireland, 14-16 May 1991, pp. 138-143.

29. Junge, C. E., "Basic Considerations About Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants," in *Fate of Pollutants in the Air and Water Environments, Part I, Mechanism of Interaction Between Environments and Mathematical Modeling and the Physical Fate of Pollutants,* I. H. Suffet, editor, John Wiley and Sons, New York, NY, pp. 7-25, 1977.

30. Broecker, W. S., and Peng, T. H., "Gas Exchange Rates Between Air and Sea," *Tellus,* Vol. 26, pp. 21-35, 1974.

31. Himmelblau, D. M., "Diffusion of Dissolved Gases in Liquids," *Chemical Reviews,* Vol. 64, pp. 527-550, 1964.

32. Sax, N. I., and Lewis, R. J., Sr., *Dangerous Properties of Industrial Materials,* Seventh Edition, Van Nostrand Reinhold, New York, NY, 1989.

33. *Registry of Toxic Effects of Chemical Substances,* Sweet, D. V., editor, U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health, Washington, DC, Report Number DHHS (NIOSH) 87-114, Vols. 1-5, April, 1987.

34. Larsen, E. R., "Fluorine Compounds in Anaesthesiology," in *Fluorine Chemistry Reviews,* P. Tarrant, editor, Marcel Dekker, New York, pp. 1-44, 1969.

35. Hodgson, E., Mailman, R. B., and Chambers, J. E., *Dictionary of Toxicology,* Van Nostrand Reinhold Company, NY, p. 243, 1988.

36. "NFPA 2001 Standard on Clean Agent Fire Extinguishing Systems 1994 Edition," National Fire Protection Association, 1 Batterymarch Park, Quincy Massachusetts, 11 February 1994.

37. "NFPA 2001 Standard on Clean Agent Fire Extinguishing Systems 1996 Edition," National Fire Protection Association, 1 Batterymarch Park, Quincy, Massachusetts.

38. *Federal Register,* Vol. 59, No. 53, pp. 13044-13161, March 18, 1994.

39. 29 CFR 1910.162, U.S. Government Printing Office, Washington, DC, 1981.

40. Tapscott, R. E., Skaggs, S. R., and Dierdorf, D. S., "Perfluoroalkyl Iodides and Other New Generation Halon Replacements," in *Halon Replacements Technology and Science,* A. W. Miziolek and W. Tsang, editors, American Chemical Society, Washington, DC, pp. 151-160, 1995.

41. Skaggs, S. R., Dierdorf, D. S., and Tapscott, R. E., "Update on Iodides as Fire Extinguishing Agents," *Proceedings, International CFC and Halon Alternatives Conference*, Washington, D.C., 20-22 October 1993, pp. 800-809.

42. Tapscott, R. E., "Update on Iodides as Second-Generation Halon Replacements," International Halon Replacement Working Group Meeting, The Fire Service College, Moreton-in-Marsh, England, UK, 14-15 March 1994.

43. Moore, T. A., Skaggs, S. R., Corbitt, M. R., Tapscott, R. E., Dierdorf, D. S., and Kibert, C. J., *The Development of CF$_3$I as a Halon Replacement*, WL-TR-94-XXX, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, November 1994. NMERI 1994/40

44. Solomon, S., Burkholder, J. B., Ravishankara, A. R., and Garcia, R. R., "Ozone Depletion and Global Warming Potentials of CF$_3$I," *Journal of Geophysical Research*, Vol. 99, pp. 20929-20935, 20 October 1994.

45. Lifke, J. L., Moore, T. A., and Tapscott, R. E., *Advanced Agent Program: CF$_3$I Blends*, WL-TR-96-XX, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, May 1995. NMERI 1995/19/31882 (Draft)

46. Tapscott, R. E., Moore, T. A., Skaggs, S. R., and Heinonen, E. W., *Fluoroiodide Blends as Streaming Agents: Selection Criteria and Cup-Burner Results*, WL-TR-95-XX, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1995. NMERI 1995/8/31790

47. *Acute Inhalation Toxicity Study of Iodoheptafluoropropane in Rats*, Final Report, Project No. 1530-001, Study No. 3, ManTech Environmental Technology, Inc., Research Triangle Park, North Carolina, 1994.

48. Lifke, J. L., Moore, T. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests*, WL-TR-96-XX, Vol. 5 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/2/32540 (Draft)

49. Pitts, W. M., Nyden, M. R., Gann, R. G., Mallard, W. G., and Tsang, W., *Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives*, NIST Technical Note 1279, Air Force Engineering and Services Laboratory, Tyndall Air Force Base, Florida, National Institute of Standards and Technology, Gaithersburg, Maryland, August 1990.

50. Kobayashi, Y., Yamamoto, K., and Kumadaki, I., "Trifluoromethylation of Aliphatic Halides With Trifluoromethyl Copper," *Tetrahedron Letters*, pp. 4071-4972, 1979.

51. McLoughlin, V. C. R., and Thrower, J., "A Route To Fluoroalkyl-Substituted Aromatic Compounds Involving Fluoroalkylcopper Intermediates," *Tetrahedron*, Vol. 25, pp. 5921-5940, 1969.

52. Pawelke, G., Dammel, R., and Poll, W., "Darstellung von Difluormethanimin $F_2C=NH$ und $F_2C=ND$ durch Hydrolyse von CF_3NCO," *Zeitschrift für Naturforschung B*, Vol. 47, pp. 351-357, 1992.

53. Hendry, D. G., and Kenley, R. A., *Atmospheric Reaction Products of Organic Compounds*, EPA-560/12-79-001, Office of Chemical Control, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC, June 1979.

54. Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, April 1996. NMERI 96/1/32540 (Draft)

55. Abreu, B. E., *Anesthesiology*, Vol. 2, p. 393, 1941.

56. Manahan, S. E., *Toxicological Chemistry*, Lewis Publishers, Inc., Chelsea, Michigan, 1989.

57. Prakash, G. K. S., Krishnamurti, R., and Olah, G. A., "Fluoride-Induced Trifluoro-methylation of Carbonyl Compounds with Trifluoromethyltrimethylsilane (TMS-CF3). A Trifluoromethide Equivalent," *Journal of the American Chemical Society*, Vol. 111, pp. 393-395, 1989.

58. Francisco, J. S., "An Examination of Primary and Secondary Dissociation Pathways of Trifluoromethanol: Identification of Plausible Routes Leading to The Formation of Hydrogen Fluoride," *Chemical Physics*, Vol. 150, pp. 19-27, 1991.

59. Wallington, T. J., and Schneider, W. F., "The Stratospheric Fate of CF_3OH," *Environmental Science and Technology*, Vol. 28, pp. 1198-1200, 1994.

60. Francisco, J. S., *Chemical Physics*, Vol. 150, 1991, pp. 19-27.

61. Rattigan, O., Cox, R. A., and Jones, R. L., "The UV Absorption Cross-Sections of CF_3COCl, CF_3COF, CH_3COF, and CCl_3CHO," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 116-125.

62. Sittig, M., *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, Noyes Publications, Park Ridge, New Jersey, 1985.

63. Klink, F. W., Minday, R. M., Owens, J. G., and Flynn, R. M., "New Fluorinated Alternatives to Ozone Depleting Substances," International CFC and Halon Alternatives Conference, Washington, DC, 24-26 October 1994.

64. Gillis, K. A., "Thermodynamic Properties of Two Gaseous Halogenated Ethers from Speed-of-Sound Measurements: Difluoromethoxy-Difluoromethane and 2-Difluoro-methoxy-1,1,1-Trifluoroethane," *International Journal of Thermophysics*, Vol. 15, pp. 821-847, 1994.

65. McLinden, M. O., and Didion, D. A., "Quest for Alternatives - A Molecular Approach Demonstrates Tradeoffs and Limitations are Inevitable in Seeking Refrigerants," *ASHRAE Journal*, Vol. 28, p. 32, 1987.

66. *Dictionary of Organic Compounds*, Fifth Edition, Chapman and Hall, New York, 1987.

67. Smith, N. D., Ratanaphruks, K., Tufts, M. W., and Ng, A. S., "HFC-236ea: A Potential Alternative for CFC-114," *Proceedings, International CFC and Halon Alternatives Conference*, Washington, DC, 20-23 October 1993, pp. 150-157.

68. Smith, N. D., Rantanaphruks, K., Tufts, M. W., and Ng, A. S., "R-245ca: A Potential Far-Term Alternative for R-11," *ASHRAE Journal*, pp. 19-23, 1993.

69. *Aldrich General Catalog, 1994-1995*, Aldrich Chemical Company, Milwaukee, Wisconsin, 1994.

70. Takahashi, K., Inomata, T., Fukaya, H., and Abe, T., "New Halon Replacements Based on Perfluoroalkylamines. An Approach from the Other Side of Fluorine Chemistry," in *Halon Replacements Technology and Science*, ACS Symposium Series 611, Miziolek, A. W., and Tsang, W., editors, American Chemical Society, Washington, DC, Chapter 13, pp. 139-150, 1995.

71. Takahashi, K., Sekiuji, Y., Inomata, T., Abe, T., Fukaya, H., Hayashi, E., and Inoue, G., "Inhibition of Combustion by Bromine-Free Polyfluorocarbons I. Burning Velocities of Methane Flames Containing Polyfluoroalkylamines," *Combustion Science and Technology*, Vol. 102, pp. 213-230, 1994.

72. Fukaya, H., Ono, T, and Abe, T., "New Fire Suppression Mechanism of Perfluoroalkylamines," *Journal of Chemical Society Chemical Communications*, pp. 1207-1208, 1995.

73. Brabson, G. D., Spencer, C., Schiro, J., Walters, E. A., and Patterson, R. A., "Role of •CF$_3$ Radical in Extinguishment," Proceedings, Halon Options Technical Working Conference, Albuquerque, New Mexico, 7-9 May 1996, pp. 611-613.

74.	Abe, T., Hayashi, E., Fukaya, H., and Hayakawa, Y., "The Electrochemical Fluorination of Nitrogen-Containing Carboxylic Acids. Fluorination of Methyl Esters of 3-Dialkylamino Propionic Acids," *Journal of Fluorine Chemistry*, Vol. 57, pp. 101-111, 1992.

75.	Fukaya, H., Abe, T., and Hayashi, E., "Convenient Synthesis of N-Containing Perfluoroalkyl Iodides," *Chemistry Letters*, pp. 813-814, 1990.

76.	McMillen, D. F., and Golden, D. M., *Annual Reviews of Physical Chemistry*, Vol. 33, p. 493, 1982.

77.	Seyferth, D, and Hopper, S. P., Halomethyl-Metal Compounds LXI. Phenyl(fluorodibromomethyl)mercury, a Fluorobromocarbene Precursor," *Journal of Organometallic Chemistry*, Vol. 51, 1973, pp. 77-87.

78.	Behnke, W., and Zetsch, C., "The Photodegradation of Trichloroacetyl Chloride and Trichloroacetic Acid in an Aerosol Smog Chamber," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 144-149.

79.	Libuda, H. G., Zabel, F., and Becker, K. H., "UV Spectra of Some Organic Chlorine and Bromine Compounds of Atmospheric Interest," *Proceedings, STEP - HALOCSIDE/AFEAS Workshop, Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, Dublin, Ireland, 14-16 May 1991, pp. 126-131.

80.	"Flame Retardants Seek Uses in Broader Resin Spectrum," *Plastics Technology*, Vol. 41, pp. 21, 23, 25-28, September 1995.

81.	Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesa, G., and Davis, D. D., *International Journal of Chemical Kinetics*, Vol. 10, pp. 783-804, 1978.

82.	Tapscott, R. E., and Skaggs, S. R., *Identification of Alternatives to CFC-113 for Solvent Cleaning*, NASA White Sands Test Facility, Las Cruces, New Mexico, September 1994. NMERI 1994/41

83.	The *Condensed Chemical Dictionary*, 8th Edition, Revised by G. G. Hawley, Van Nostrand Reinhold Company, New York, 1971, p. 103.

84.	Burns, T. H. S., Hall, J. M., Bracken, A., and Gouldstone, G., *Anaesthesia*, Vol. 19, p. 167, 1964.

85.	Burns, T. H. S., Hall, J. M., Bracken, A., and Gouldstone, G., *Anaesthesia*, Vol. 16, p. 333, 1961.

APPENDIX A
HALOCARBON NOMENCLATURE

The following has been taken verbatim from a report that is not widely available (*Halocarbon Nomenclature*, CGET3, Center for Global Environmental Technologies, University of New Mexico, Albuquerque, New Mexico, February 1996. NMERI 1995/22). For that reason, it has been duplicated here with the permission of the Center for Global Environmental Technologies at The University of New Mexico.

IUPAC NOMENCLATURE

The International Union of Pure and Applied Chemistry (IUPAC) has developed rules for naming organic compounds. It is assumed that the reader is familiar with the basics of these rules. The following is only a brief overview of some of the points about the IUPAC system of particular importance to naming halocarbons.

In the IUPAC naming system, each substituent is assigned a number giving its position on the molecule, unless no ambiguity is caused omitting the number. For example, fluoroethane, CH_3CH_2F, requires no numbering since the same compound results no matter where the fluorine atom is place. On the other hand, 1-fluoropropane, $CH_2FCH_2CH_3$, requires a number to distinguish it from 2-fluoropropane, CH_3CHFCH_3. If more than one of a given substituent is present, the prefixes di-, tri-, tetra-, penta-, and so forth are used.

The carbon chain of the molecule is numbered to give the lowest sum of numbers to the substituents. For example, the molecule $CH_2ClCHClCHCl_2$ is named 1,1,2,3-tetrachloropropane (numbered from the right), not 1,2,3,3-tetrachloropropane. If the numbering (and therefore the sum of substituent numbers) would be the same from either end, the first group alphabetically takes priority. For example, CH_2FCH_2I is named 1-fluoro-2-iodoethane (not 2-fluoro-1-iodoethane). Similarly, because chlorine comes before fluorine in the alphabet, the compound $CHF_2CHClCHClF$ is designated 1,2-dichloro-1,3,3-trifluoroethane (not 2,3-dichloro-1,1,3-trifluoroethane) even though the set of numbers is the same (1,1,2,3,3) from either end of the molecule.

Prefixes such as di-, tri-, tetra-, etc. are ignored in the alphabetization of substituents. These prefixes are inserted after the substituent names, such as "bromo," "chloro," "fluoro," and "iodo," have been alphabetized. Therefore, "bromo" always comes before "chloro," no matter how many of each are present. For example the compound $CHBr_2CBrCl_2$ is named 1,2,2-tribromo-1,1-dichloroethane (not 1,1-dichloro-1,2,2-tribromoethane).

If a conflict in priority between numbering and alphabetization occurs, numbering takes precedence. The carbon atoms are numbered to give the lowest set of substituent numbers, instead of the lowest number going to the carbon with the first alphabetical substituent. For example, $CHCl_2CF_3$ is called 2,2-dichloro-1,1,1-trifluoroethane, the lowest set of numbers taking priority. It would be incorrect to name this compound 1,1-dichloro-2,2,2-trifluoroethane, giving priority in numbering carbon atoms to the substituent names.

The prefix "per" indicates that every possible site on the carbon skeleton is occupied by the same type of substituent. For example, perfluoropropane is $CF_3CF_2CF_3$.

112

HALOCARBON NUMBERING SYSTEM

It has become a general practice within the refrigeration industry to designate various halocarbons with a number. This "Halocarbon Numbering System" has now become widely used, and an unofficial extended version has been used in both national and international regulations. The Halocarbon Numbering System (sometimes called the CFC, Freon®, or Refrigerant Numbering System) was developed by DuPont for Freon® chemicals in the late 1930s. The system was later expanded and formalized into a standard by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) and the American National Standards Institute (ANSI) (Reference 1). Note, however, that this Standard uses the Halocarbon Numbering System only for derivatives of cyclobutane, propane, ethane, and methane. The unofficial, but widely used, extended numbering system described in this document is applicable for larger molecules; however, this will give numbers that could conflict with refrigerant numbers assigned to other chemicals (particularly, blends or inorganics).

In the early days, many of the halocarbon chemicals used as refrigerants were given numbers preceded by the designation "Freon®"; however, since this is a trade name, other prefixes are now usually used. In the refrigeration industry, it is common practice to precede the Halocarbon Number with an "R." However, such a prefix can be misleading for refrigerants other than butane, propane, ethane, or methane derivatives. A series of letters denoting the type of compound is now often used. For example, compounds containing only chlorine and fluorine (in addition to carbon) have numbers preceded by "CFC," which stands for "chlorofluorocarbon." Though not universally accepted or standardized, other prefixes are being increasingly used. Table 1 lists the prefixes that have been adopted. Note that two prefixes are used for perfluorocarbons: "FC" and "PFC." Note also that this prefix nomenclature is beginning to be used for ethers. Thus "HFE" denotes a hydrofluoroether.

In the Halocarbon Numbering System, the first number gives the number of carbon atoms minus one, followed by (in order) the number of hydrogen atoms plus one and the number of fluorine atoms:

first number	number of carbon atoms - 1
second number	number of hydrogen atoms + 1
third number	number of fluorine atoms

All remaining atoms are assumed to be chlorine atoms. An initial zero (indicating a one-carbon compound) is omitted. For example, CFC-12 has one carbon atom (the initial zero has been dropped), no hydrogen atoms (0 + 1 = 1), two fluorine atoms and, by default, two chlorine atoms, for a formula CF_2Cl_2. CFC-113 is CF_3CCl_3 or one of its isomers. When any number in the halocarbon designation contains two or more digits, dashes are used to separate the numbers. For example, $CF_3CF_2CF_2CF_2CClF_2$ is CFC-4-1-11 (ignoring isomer designations discussed below). It has been suggested that dashes be used only to set off the specific numbers with multiple digits, but this could be misleading. For example, CFC-41-11 could correspond to a 5-carbon compound or a 42-carbon compound (admittedly, unlikely).

Table 1. Prefixes for Halocarbon Numbers.

[a]Prefix	Elements in Chemical	Chemical Family
BC	Br, C	Bromocarbon
BCC	Br, Cl, C	Bromochlorocarbon
BCIC	Br, Cl, I, C	Bromochloroiodocarbon
BCFC	Br, Cl, F, C	Bromochlorofluorocarbon
BCFIC	Br, Cl, F, Cl, C	Bromochlorofluoroiodocarbon
BFC	Br, F, C	Bromofluorocarbon
BFIC	Br, F, I, C	Bromofluoroiodocarbon
BIC	Br, I, C	Bromoiodocarbon
CC	Cl, C	Chlorocarbon
CFC	Cl, F, C	Chlorofluorocarbon
CFIC	Cl, F, I, C	Chlorofluoroiodocarbon
CIC	Cl, I, C	Chloroiodocarbon
FC	F, C	(Per)fluorocarbon
FE	F, C, O	(Per)fluoroether
FIC	F, I, C	Fluoroiodocarbon
HBC	H, Br, C	Hydrobromocarbon
HBCC	H, Br, Cl, C	Hydrobromochlorocarbon
HBCFC	H, Br, Cl, F, C	Hydrobromochlorofluorocarbon
HBCFIC	H, Br, Cl, F, I, C	Hydrobromochlorofluoroiodocarbon
HBCIC	H, Br, Cl, I, C	Hydrobromochloroiodocarbon
HBFC	H, Br, F, C	Hydrobromofluorocarbon
HBFIC	H, Br, F, I, C	Hydrobromofluoroiodocarbon
HBIC	H, Br, I, C	Hydrobromoiodocarbon
HC	H, C	Hydrocarbon
HCC	H, Cl, C	Hydrochlorocarbon
HCFC	H, Cl, F, C	Hydrochlorofluorocarbon
HCFIC	H, Cl, F, I, C	Hydrochlorofluoroiodocarbon
HCIC	H, Cl, I, C	Hydrochloroiodocarbon
HFC	H, F, C	Hydrofluorocarbon
HFIC	H, F, I, C	Hydrofluoroiodocarbon
HFE	H, F, C, O	Hydrofluoroether
HIC	H, I, C	Hydroiodocarbon
IC	I, C	Iodocarbon
PFC	F, C	Perfluorocarbon
PFE	F, C, O	Perfluoroether

[a]For cyclic compounds, the prefix "C" precedes the Halocarbon Number. For example, perfluorocyclobutane (cyclo-C_4F_8) is FC-C318. For unsaturated compounds, a number giving the number of double bonds is added on the left, e.g., $CF_2=CClF$ is CFC-1113. The presence of four numbers (may be more than four digits) always denotes an unsaturated compound.

TWO-CARBON COMPOUNDS (ETHANE AND ETHENE DERIVATIVES)

When there are two (or more) carbon atoms present, isomers are possible, and these may have identical Halocarbon Numbers. To distinguish these isomers for ethane derivatives, a lower case letter is added based on the difference in the sum of the atomic masses of the carbon substituents. The designation for the isomer with the smallest difference in the sum of the masses on the two carbon atoms has no letter; the designation corresponding to the next smallest difference has an "a", the next a "b", etc. Some examples are given below for the isomers of dichlorodifluoroethane.

$CHClFCHClF$	HCFC-132
$CHCl_2CHF_2$	HCFC-132a
$CClF_2CH_2Cl$	HCFC-132b
CCl_2FCH_2F	HCFC-132c

If bromine is present in the molecule, the Halocarbon Number is first assigned as if the bromine atoms were chlorine atoms (i.e., the Halocarbon Number is assigned for the "parent" molecule). The designation "Bn," where "n" is the number of bromine atoms, is then added to the end of the Halocarbon Number. For example, the anesthetic Halothane ($CF_3CHBrCl$) is HBCFC-123B1. The absence of a small letter indicates that this is the most symmetrical isomer, and the final "B1" means that one of the chlorine atoms was replaced with a bromine. The parent compound in this case is CF_3CHCl_2 (HCFC-123). As another example, $CClF_2CHBrF$, parent compound $CClF_2CHClF$, is HBCFC-123aB1 (omitting a final suffix for the bromine position, which is discussed below). CGET/NMERI has extended this further to include iodine compounds using a suffix "In," where "n" is the number of iodine atoms. This extension gives FIC-12I2 for CF_2I_2 and BFIC-12B1I1 for CF_2BrI.

Where the positions of the bromine atoms are ambiguous, Greek letter suffixes are added. The letters "α," and "β" denote the carbon atoms in the chain starting from the end carbon having the highest sum of atomic weights in the parent compound. HBCFC-123aB1 exists as two isomers — HBCFC-123aB1α ($CBrF_2CHClF$) and HBCFC-123aB1β ($CClF_2CHBrF$). Similarly, $CBrClFCBrF_2$ is HBCFC-113B2$\alpha\beta$ and CBr_2FCClF_2 is HBCFC-113B2$\alpha\alpha$. NMERI/CGET has extended this to iodine-containing compounds: $CF_2ICHClF$ is HCFIC-123aI1 α, $CClF_2CHFI$ is HCFIC-123aI1ß, $CClFICF_2I$ is CFIC-113I2αß, and CFI_2CClF_2 is CFIC-113I2α α. Where both bromine and iodine are present, the Greek letter position designations are placed after the appropriate designations giving the number of bromine and iodine atoms. For example, $CClFICBrF_2$ is BCFIC-113B1ßI1α and $CBrClFClF_2$ is BCFIC-113B1αI1ß.

THREE-CARBON COMPOUNDS (PROPANE AND PROPENE DERIVATIVES)

The Halocarbon Numbering System for three-carbon compounds (propanes) is similar to that for two-carbon compounds; however, two letters are required to specify the isomer. (Letters are omitted when there is no possibility of isomerism.) The first letter refers to the central

(methylene) carbon atom of the propane. To assign this letter, one calculates the combined atomic mass of the substituents on this carbon atom in the parent compound (containing only H, F, and/or Cl). The letter "a" represents the largest mass possible, the letter "b," the next largest, etc. The letters are assigned as shown in Table 2.

Table 2. Methylene Carbon Designations.

Suffix	Chemical Group
a	$-CCl_2-$
b	$-CClF-$
c	$-CF_2-$
d	$-CHCl-$
e	$-CHF-$
f	$-CH_2-$

The second letter is determined by the difference in the combined atomic masses of the substituents on the two terminal carbon atoms. The smallest difference is assigned the letter "a," the next smallest difference is assigned the letter "b," followed by "c," "d," etc. This method of isomer designation differs from that for two-carbon compounds, in which the smallest difference has no letter. For example, $CHCl_2CF_2CF_3$ (3,3-dichloro-1,1,1,2,2-pentafluoropropane) is designated HCFC-225ca, and the isomer $CHClFCF_2CClF_2$ (1,3-dichloro-1,1,2,2,3-pentafluoropropane) is HCFC-225cb.

If a three-carbon compound contains bromine or iodine, the suffix "Bn" or "In" is added as done for methane and ethane derivatives. Where the position of the bromine atom is ambiguous, Greek letter suffixes are again added. The letters "α," "β," and "γ" denote the carbon atoms in the chain starting from the end carbon having the highest sum of atomic weights in the parent compound. Thus, $CF_3CBrClCH_2Br$ (parent compound, $CF_3CCl_2CH_2Cl$) is HBCFC-233abB2ßγ and $CF_3CHClCHI_2$ (parent compound $CF_3CHClCHCl_2$) is HBCFC-233daI2 αα. Application to mixed bromine/iodine derivatives is obvious: $CF_3CFBrCF_2I$ is BFIC-216baB1ßI1α, $CF_3CFICBrF_2$ is BFIC-216baB1αI1ß, and $CF_3CBrICF_3$ is BFIC-216aaB1I1. Note that the last compound is not designated as BFIC-216aaB1ßI1ß since the iodine and bromine must reside on the central atom for a compound with the Halocarbon Number 216aa. Isomer designation letters for both the parent compound and for the bromine or iodine positions are always omitted when no ambiguity can result.

Halocarbon designations for propenes contain four numbers starting with 1 (one double bond) and two lower case letter suffixes. The first suffix designates the single atom attached to

116

the central atom (methine group, Table 3). The second letter gives the substitution on the terminal methylene carbon atom using the same letter designations as used for the central methylene carbon on propane derivatives (Table 2). Thus, $CH_2=CHCF_2Cl$ is HCFC-1242zf. Bromo- and iodopropenes are designated in the same way as for bromo- and iodopropanes and bromo- and iodoethanes (i.e., with suffixes "Bn" and "In." Greek letters are added where necessary starting with the methylene end. Thus $CHBr=CBrCF_2Cl$ (parent compound, $CH_2=CClCF_2Cl$) is HCFIC-1232zfB2 (no Greek Letter descriptor is needed since the positions of the bromine atoms are fixed by the Halocarbon Number) and $CHI=CBrCF2Cl$ is HCFIC-1232zfB1βI1α.

Table 3. Methine Carbon Designations.

Suffix	Chemical Group
x	$-\overset{\textstyle |}{\underset{\textstyle |}{C}}Cl$
y	$-\overset{\textstyle |}{\underset{\textstyle |}{C}}F$
z	$-\overset{\textstyle |}{\underset{\textstyle |}{C}}H$

COMPOUNDS WITH FOUR OR MORE CARBON ATOMS

Compounds with four or more carbon atoms are coded in a way similar to that used for compounds with fewer carbon atoms. To differentiate between isomers, carbon atoms containing a single substituent (methine carbons) are designated as shown in Table 3, carbon atoms with two substituents (methylene carbons) as shown in Table 2, and methyl groups as in Table 4. Letter designations begin at one end of the molecule (chosen to keep the alphabetical sequence as low as possible) for linear compounds. Bromine- and/or iodine-substituted compounds are handled in a fashion similar to that used for compounds with three or fewer carbon atoms.

117

Table 4. Methyl Group Designations.

Suffix	Chemical Group
j	$-CCl_3$
k	$-CCl_2F$
l	$-CClF_2$
m	$-CF_3$
n	$-CHCl_2$
o	$-CH_2Cl$
p	$-CHF_2$
q	$-CH_2F$
r	$-CHClF$
s	$-CH_3$
t	$-C$

Some examples for larger molecules are shown in Table 5. Note again that isomer designation letters not needed to describe a structure are omitted. Thus, $CCl_3CCl_2CCl_2CCl_2CCl_3$ is designated as CC-410 and not as CC-410jaaaj. Similarly, $CCl_3CF_2CF_2CF_2CF_3$ is CFC-4-1-9j; no additional letters are needed to describe the structure.

Table 5. Examples for Compounds with Four or More Carbon Atoms.

Compound	Halocarbon Number
$CCl_3CCl_2CCl_2CCl_2CCl_3$	CC-410
$CCl_3CF_2CF_2CF_2CF_3$	CFC-4-1-9j
$CF_3CClFCH_2CH_2F$	HCFC-355mb
$CF_3CBrFCH_2CH_2F$	HBFC-355mbfB1
$CF_3CHFCHFCF_2CF_3$	HFC-4-3-10mee
$CF_3CF_2CH_2CH_2F$	HFC-356mcf

ETHERS

Rules have been proposed for numbering ether-based refrigerants (Reference 2). Usually ether designations have an "E" or "CE" (in the case of cyclic ethers) immediately preceding the number; however, to avoid redundancy, the E immediately preceding the number is omitted here. For dimethylether derivatives, designation numbers are derived in the same way as those for the haloethanes. For straight-chain, three-carbon derivatives, the carbon atoms are numbered sequentially with "1" assigned to the end carbon with the least number of halogen atoms. When the end carbon atoms contain the same number of halogen atoms, number 1 is assigned to the end carbon having the largest number of iodine, then bromine, then chlorine, and finally fluorine atoms. The number giving the location of the ether oxygen is placed at the end of the suffix letters, which are retained when a single isomer exists. Some examples follow: $CF_3OCF_2CF_3$, FE-218ca1; $CHF_2OCHClCHF_2$, HCFE-244da1; and $CF_3OCH_2CHF_2$, HFE-245fa2. We can modify the proposed rules to include molecules containing four or more carbon atoms by using the method shown in the previous section, but starting with the end carbon containing the least number of halogen atoms. For example, $CF_3CF_2CF_2CF_2OCH_3$ is HFE-449s1 and $CF_3CF_2CF_2CF_2OCH_2CH_3$ is HFE-569sf2. Nomenclature rules have been proposed for only 3-carbon cyclic ethers. For such compounds, the oxygen atom is taken to be positioned between C1 and C3. Thus, $-CF_2CHFCF_2O-$ is HFE-CE225ea.

HALON NUMBERING SYSTEM

An alternate numbering system, the Halon Numbering System, is often used for fire extinguishing agents, particularly those containing bromine. This designation system is sometimes used for materials other than fire extinguishants. The Halon Numbering System designation lists, in order, the number of carbon, fluorine, chlorine, and bromine atoms in a molecule. NMERI/CGET has extended this convention to add a 5th number to designate the number of iodine atoms if needed. Trailing zeros are dropped. Thus Halon 1211 is $CBrClF_2$ and Halon 1301 is $CBrF_3$. The Halon Numbering System cannot specify isomers; both $CBrF_2CBrF_2$ and CF_3CBr_2F are designated Halon 2402. The Halon Numbering System is not used for cyclic or unsaturated compounds.

NMERI/CGET HALOCARB© COMPUTER PROGRAM

NMERI/CGET has developed a computer code written in BASIC language that determines the IUPAC name, Halocarbon Number, halon number, and molecular weight for halocarbons from the structural formula. A copy of the compiled DOS program, HALOCARB.EXE©, is available on request.

To start the program, type "HALOCARB.EXE" from the A>, B>, or C> prompt depending on the drive containing the program. The program will then ask for a structural formula of the compound. The structural formula can be entered in any order and with any combination of capital and lower case letters. Numbers normally subscripted are entered as unsubscripted. A carbon atom must be entered first ("C" or "c") followed by the elements attached to that carbon atom. This process is repeated for each carbon atom. For example, the compound $CHClFCF_3$, HCFC-124, could be entered as "chclfcf3," "cf3cfclh," "cHcLfCf3," etc. For this example, the formula cannot be input as "C2HCLF4" (the structural formula rather than the empirical formula must be used) or as "CHCLFCFFF" (subscripts and not repeated letters must be used). If an impossible or unrecognized entry is given, the program will give an error message and will ask for a re-entry. The program will return the halon number, the Halocarbon Number (with the right isomer designation), the proper IUPAC name, and the molecular weight. Upon completion for one compound, the program asks for a new entry for another compound. At this point, a new structural formula can be entered or execution can be terminated by entering "Q." This program has been thoroughly checked out and is believed to be accurate. The present version will not handle unsaturated, cyclic, or branched-chain compounds. Nor will it give isomer designation for compounds containing four or more carbon atoms. These features are being added to a new version under development.

One word of caution is that the program will assign Halocarbon Numbers to any molecule with up to 9 carbon atoms. This will give a number corresponding to the appropriate refrigerant number in ASHRAE Standard 34 for propane, ethane, and methane halocarbon derivatives; however, for derivatives of pentane, hexane, and higher hydrocarbons, numbers are obtained that do not correspond to the refrigerant numbers in the ASHRAE Standard because refrigerant numbers above 400 have been reserved for materials that are not pure halocarbons (e.g., blends and inorganics). Halocarbon Numbers and refrigerant numbers are not always the same.

REFERENCES

1. *Number Designation and Safety Classification of Refrigerants*, ANSI/ASHRAE Standard 34-1992, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Georgia, 1992.

2. Dekleva, T., "Recommended Convention for Naming Ether Refrigerants," Nomenclature Subcommittee, ASHRAE SSPC 34, 20 October 1994.

APPENDIX B

GLOSSARY

Aliphatic—Straight-chain, branched-chain, or cyclic structures containing carbon atoms linked by single sp^3-sp^3 bonds.

Alkoxy—A group of the type -OR, where R is an aliphatic hydrocarbon radical or a substituted aliphatic group. Examples are methoxy ($-OCH_3$) and ethoxy ($-OC_2H_5$).

Alkene—A compound containing doubly bonded carbon atoms (excluding aromatic compounds). Examples are ethene ($H_2C=CH_2$) and propene ($H_2C=CHCH_3$).

Alkyl—An aliphatic substituent. Examples are methyl ($-CH_3$), ethyl ($-CH_2CH_3$ or $-C_2H_5$), *n*-propyl ($-CH_2CH_2CH_3$ or $-C_3H_7$), *i*-propyl ($-CH(CH_3)_2$), *n*-butyl ($-CH_2CH_2CH_2CH_3$ or $-C_4H_9$), *t*-butyl ($-C(CH_3)_3$).

Aromatic—Cyclic molecules or fused cyclic molecules containing formally alternating single and double bonds with delocalized π electrons. The most common simple aromatic compound is benzene.

Aryl—Aromatic substituents derived from benzene and related compounds. Examples are phenyl ($-C_6H_5$), tolyl ($-C_6H_4CH_3$), and naphthyl ($-C_{10}H_7$).

Ester—A compound formed from an alcohol and an oxyacid by elimination of water.

Geminal—Two atoms that are located on the same carbon atom are said to be geminal.

Halocarbon—A compound of carbon and one or more halogen atoms with or without hydrogen.

Halogen—One of the elements or atoms fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The last element is radioactive and is not considered in this project.

Hydrocarbon—A binary compound of carbon and hydrogen. This term includes aliphatic compounds (paraffins), compounds containing double bonds (olefins), and aromatics.

Hydrochlorofluorocarbon—An aliphatic compound containing only hydrogen, fluorine, chlorine, and carbon. An example is HCFC-123, $CHCl_2CF_3$.

Hydrofluorocarbon—An aliphatic compound containing only hydrogen, fluorine, and carbon. An example is HFC-134a, CH_2FCF_3.

Hydroxyl—The -OH group, common to alcohols, ROH, and water or the unattached •OH free radical.

Perfluorocarbon—An aliphatic compound containing only fluorine and carbon. An example is FC-218 (sometimes called PFC-218), $CF_3CF_2CF_3$.

Pi (π) Bonding—Bonding involving "sideways" overlap of atomic orbitals as opposed to sigma (σ) bonding.

Sigma (σ) Bonding—Bonding involving direct, end-on overlap of atomic orbitals.